Experimental Section

All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with N_2 followed by passage through an activated alumina column. Non-halogenated solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. Deuterated solvents were degassed and stored over activated 3-Å molecular sieves prior to use. THF-*d8* was dried by passage over activated alumina and stored over activated sieves prior to use. $LiP(^{i}Pr)_2$[1] was prepared according to literature procedures. All other reagents were purchased from commercial vendors and used without further purification, unless explicitly stated. Elemental analysis was carried out at Desert Analytics, Tucson, Arizona. NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz or Inova Automated 500 MHz spectrometer. ^{1}H NMR chemical shifts were referenced to residual solvent. ^{31}P NMR chemical shifts are reported relative to an external standard of 85% H_3PO_4. ^{19}F NMR chemical shifts are reported relative to either a HCF_3 or C_6F_6 standard. UV-vis measurements were taken on a Varian Cary 50 Bio Spectrophotometer, using a quartz crystal cell with a Teflon stopper. Electrochemical analysis was performed on a CHI 600B Potentiostat/Galvanostat using a glassy carbon working electrode, a platinum wire auxiliary electrode, and a $Ag/AgNO_3$ (0.01 *M*) reference electrode filled with THF, with reference to Fc/Fc^{+} as an internal standard. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer. High resolution mass spectra (HRMS) were obtained at the California Institute of Technology Mass Spectral Facility. Luminescence measurements were carried out at the California Institute of Technology's Beckman Institute Laser Resource Center.

X-ray Crystallography Procedures. X-ray quality crystals were grown as indicated in the experimental procedures for each complex. The crystals were mounted on a glass fiber with Paratone-N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure.

Lifetime measurements. A solution of analyte in diethyl ether or benzene was prepared in a nitrogen filled glovebox. The quartz cuvettes (1 cm pathlength) were charged with this solution, and sealed with a Teflon stopper. Absorption spectra were acquired both before and after measurements to ensure the sample was not photodegrading. Generally, there was an insignificant amount (<1%) of photodecomposition under the experimental conditions, although there was more pronounced degradation under prolonged irradiation. Luminescence lifetime measurements were carried out as previously described[2] using 8 ns pulses (at a repetition rate of 10 Hz) from a Nd:YAG laser pumped OPO (Quanta Ray Pro, Spectra Physics). The luminescence was dispersed through a monochromator (Instruments SA DH-10) onto a photomultiplier tube (PMT) (Hamamatsu R928). The PMT current was amplified and

---

[1] Cowely, A.H.; Jones, R. H.; Mardones, M. A.; Nunn, C. M. *Organometallics,* **1991**, *10*, 1635-1637
[2] Wenger, O. S.; Henling, L. M.; Day, M. W.; Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **2004**, *43*, 2043

recorded with a transient digitizer (Lecroy 9354A). Measurements were performed at 298 K with two cuvettes of analyte solution, with excitation at λ_{ex} = 430 nm for **2**, **3**, **4**, **7**, and **8**; λ_{ex} = 440 nm for **9**; and λ_{ex} = 310 nm for **1** and **10**. Emission was collected at the wavelength, λ_{em}, specified in Table 1. The emission decay was averaged over at least 500 laser pulses, and fit to an exponential function from which k_{obs} and τ were determined. For **3** and **8**, the short-lived portion of the bi-exponential function was below the response time of the amplifier, and is approximated < 10 ns. The Zn complex **6** also had a lifetime that was too short to quantify, and so is estimated simply as < 10 ns.

Table 1. Data for Excited State Lifetime Measurements.

Sample	$\lambda_{em\ (nm)}$	k_{obs} (s^{-1})	Lifetime (τ) (μs)
223 μM **1** in Et_2O	480	$8.64x10^7$	0.012(1)
40.3 μM **2** in C_6H_6	504	$4.94x10^4$	20.2(1)
80.0 μM **3** in C_6H_6	503	(a) $4.44x10^4$	22.3(7)
		(b) n/a	< 10 ns
77.7 μM **4** in C_6H_6	533	$6.15x10^4$	16.3(3)
98.1 μM **9** in C_6H_6[a]	517	$8.76x10^6$	0.125(5)
49.6 μM **7** in C_6H_6	504	$1.50x10^5$	6.7(1)
57.4 μM **8** in C_6H_6[a]	555	(a) $6.76x10^3$	150(3)
		(b) n/a	< 10 ns

a. Sample was excited at 440 nm.

Oxidative Luminescence Quenching. Samples were prepared from two stock solutions: 34 μM **2** in C_6H_6**,** and a mixture of 34 μM **2** and 339 μM 2,6-dichlorobenzoquinone (DCQ). Using cuvettes with Teflon-separated 25 mL bulbs, solutions of varying concentrations were prepared in the cuvette, with the stock solution of **2** in the bulbs. After measurements were made on the cuvette solution, the stock solution in the bulb was mixed with the cuvette solution, diluting the concentration by a half. Luminescence lifetime measurements were taken as above. The data measurements are reported in Table 2, and a Stern-Volmer plot of k_{obs} vs. concentration of DCQ is shown in figure S1. The data is consistent with diffusion-limited electron transfer, with a rate constant, $k = 9.04x10^9\ M^{-1}s^{-1}$.

Table 2. Data for Excited State Lifetime Measurements.

Concentration of DCQ	k_{obs} (s^{-1})	Lifetime (τ, 1/ k_{obs}) (μs)
0 μM	$4.70x10^4$	21.26
11.3 μM	$1.34x10^5$	7.48
22.6 μM	$2.25x10^5$	4.44
33.8 μM	$3.51x10^5$	2.84
42.4 μM	$4.29x10^5$	2.33
68.7 μM	$6.65x10^5$	1.50
84.7 μM	$7.84x10^5$	1.27

169.5 μM	1.57×10^6	0.635

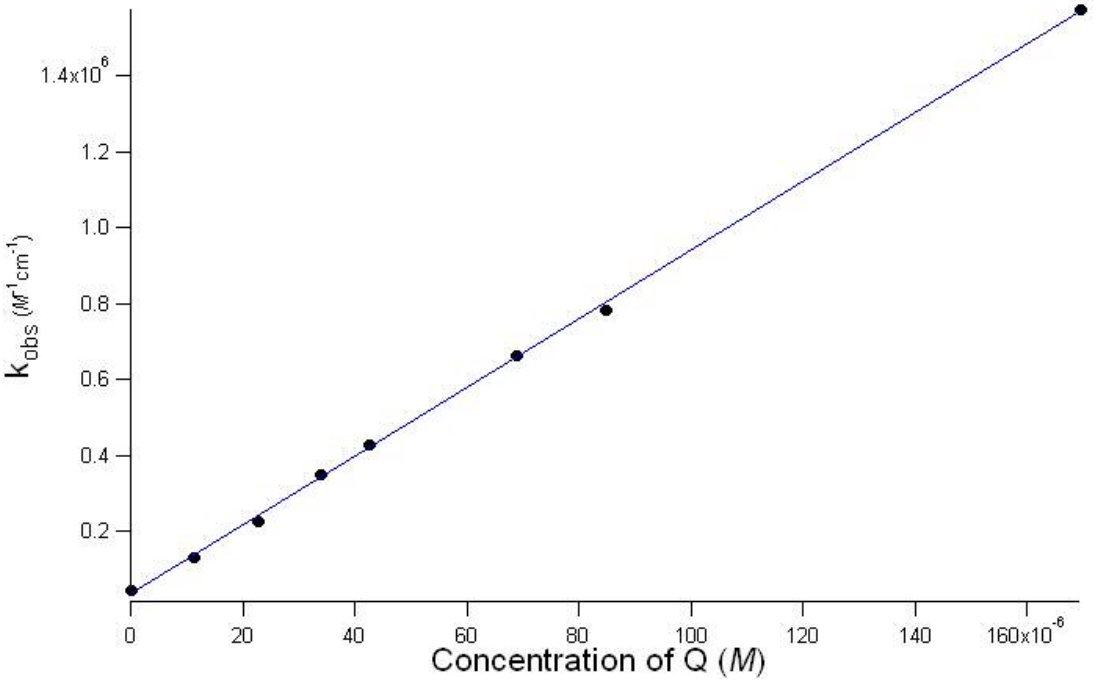

Fig. S1. Oxidative Quenching of $PNCu(PPh_3)_2$ (2) with 2,6-dibenzoquinone (Q).
$y = 9.043 \times 10^9(x) + 36767$
$R^2 = 0.9997$

Quantum yield experiments. Emission spectra were recorded on a Spex Fluorolog-2 spectro-fluorometer. A solution of analyte or reference compound in benzene, diethyl ether, tetrahydrofuran, or acetonitrile was prepared in a nitrogen filled glovebox. Cuvettes (1 cm path length) were charged with this solution and sealed with a teflon stopper. The absorption spectra were acquired both before and after fluorescence measurements to ensure the sample was not degrading. In some cases a very minor amount (<1%) of photodecomposition was observed, with more pronounced degradation under prolonged exposure to light. Fluorescence measurements were performed at the specified wavelength and corrected for detector response after equilibration to 298 K. The area under the curve of the emission spectrum was determined using standard trapezoidal integration methods. Quantum yields (Table 3) were then calculated by the methods described by Demas and Crosby[3] using eqn. I. Quinine sulfate in 0.1 N H_2SO_4[3] ($\phi = 0.54$) and $[Ru(bpy)_3][PF_6]_2$ in acetonitrile ($\phi = 0.075$)[4] were used as reference standards. Lithium salts of the ligands were prone to photodecomposition: **1** (10%), **5** (20%) and **6** (15%) all decomposed significantly after irradiation in the fluorimeter. The data is included here, but should be taken as a much more crude value.

[3] Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991
[4] Wallace, W. L.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 1350-1357.

$\phi = (QR)(I / IR)(ODR / OD)\ (\eta^2 / \eta_R^2)$ **(I)**

ϕ: quantum yield of the sample.
QR: quantum yield of reference.
I: integrated intensity of analyte.
IR: integrated intensity of reference.
ODR: optical density of the reference in absorption units.
OD: optical density of the analyte in absorption units.
η: index of refraction of the solvent in which the analyte was dissolved.
η_R: index of refraction of the solvent in which the reference was dissolved.

Table 3: Data for Quantum Yield Measurements.

Sample (solvent)	λ_{ex}	ϕ^a
1 (Et_2O)	430	0.16
2 (C_6H_6)	430	0.56
	350	0.52
2 (Et_2O)	430	0.29
2 (THF)	430	0.27
3 (C_6H_6)	430	0.21
	350	0.17
3 (Et_2O)	430	0.10
3 (THF)	430	0.05
4 (C_6H_6)	430	0.31
	350	0.36
4 (Et_2O)	430	0.15
4(THF)	430	0.05
5 (Et_2O)	430	0.12
6 (Et_2O)	430	0.05
7 (C_6H_6)	430	0.70
7 (Et_2O)	430	0.55
7 (THF)	430	0.30
8 (C_6H_6)	430	0.16
8 (Et_2O)	430	0.08
8 (THF)	430	0.07
9 (C_6H_6)	430	0.00106
10 (C_6H_6)	350	0.088

a. Quantum yields from this work are reported with confidence of ±5 on the last significant figure for measurements in benzene, and ±10 on the last two significant figures for Et_2O and THF measurements.

Preparation of complexes.

2-Fluoro-diphenylamine. In the glovebox, a 200 mL Teflon-stopped high-pressure flask was charged with Pd_2dba_3 (315 mg, 0.344 mmol; dba = dibenzylideneacetone), DPPF (275 mg, 0.688 mmol; DPPF = 1,1'-bis(diphenylphosphino)ferrocene), NaO^tBu (4.62 g, 48.16 mmol), and 80 mL toluene. The reaction flask was removed from the glovebox, and 1-bromo-2-fluorobenzene (3.74 mL, 34.4 mmol) and aniline (3.14 mL, 34.4 mmol) were added by syringe under N_2 counterflow. The mixture was heated in an oil bath at 100 °C overnight. After verifying consumption of starting materials by GC-MS and ^{19}F NMR, the mixture was cooled and filtered through a plug of silica, washing with copious petroleum ether to yield a light yellow solution. The solvents were removed *in vacuo*, yielding the desired product as a pale orange oil (5.49 g, 85%). ^1H NMR (C_6D_6, 300 MHz): δ 7.15-6.95 (m, 3H, Ar-*H*), 6.89-6.65 (m, 4H, Ar-*H*), 6.5 (m, 2H, Ar-*H*), 5.36 (br, 1H, N*H*). ^{19}F NMR (282 MHz): δ -132.5. HRMS (EI^+) *m/z* calcd. for $C_{12}H_{10}FN$: 187.0797. Found: 187.0796 [M^+], 168.0947 [M-F].

Lithium 2-(diisopropylphosphino)diphenylamide (1).[5] To a 200 mL Teflon-stopped flask charged with 20 mL of a light brown THF solution of 1-Fluoro-diphenylamine (2.20 g, 11.76 mmol), was added a 1.6 *M* hexanes solution of *n*BuLi (7.75 mL, 12.35 mmol), after which the mixture turned orange and was stirred for 20 minutes. After concentration to 5 mL, a 50 mL solution of $LiP(iPr)_2$ (2.92 g, 23.52 mmol) in THF was added, and the vessel was removed from the glove-box and heated to 65 °C for 8 days, monitoring by GC-MS and ^{19}F NMR. The mixture turned dark green over time, and was blue luminescent under a UV lamp. When no remaining starting materials were detected spectroscopically, the mixture was brought back into the glove-box, and quenched with 5 mL EtOH. After addition of 40 mL petroleum ether, the reaction mixture was filtered through celite, and the solvents were removed *in vacuo*. As it was concentrated, the oily residue formed large sticky bubbles, and the mixture was repeatedly treated with diethyl ether and then re-concentrated to control the bubbling. The residual oil was extracted with petroleum ether, and filtered through a plug of silica. Removal of solvents left a brown oil that solidified when left at ambient temperatures overnight, and was determined to be ~ 80% [PN]H by NMR, with an unknown phosphine-containing product as an impurity. Addition of *n*BuLi (7.35 mL, 11.76 mmol) to a stirring solution of the brown solids resulted in immediate precipitation of **1**, which was isolated on a sintered glass frit, and washed with copious petroleum ether, before being collected as a spectroscopically pure, thermally unstable off-white powder (2.15 g, 64%). ^1H NMR (300 MHz, THF-d^8): δ 7.04 (m, 1H, Ar-*H*), 6.88 (m, 3H, Ar-*H*), 6.73 (m, 3H, Ar-*H*), 6.26 (t, 1H, Ar-*H*), 6.12 (t, 1H, Ar-*H*), 2.02 (m, 2H, C*H*(CH_3)$_2$), 1.11, (q, 6H, CH(C*H*$_3$)$_2$), 0.98 (q, 6H, CH(C*H*$_3$)$_2$). ^{31}P NMR (120 MHz): δ -6.03 (q, 1P). HRMS (EI^+) *m/z* **c**alcd. for

[5] Lithium amides **1**, **5**, and **6** were thermally unstable and yielded repeatedly unacceptable elemental analysis results; protonolysis with EtOH yielded the corresponding amines, which were analyzed by HRMS.

$C_{18}H_{24}NP$ ([PN]H): 285.1646. Found: 285.1637 [M^+], 243.1072 [M-^{i}Pr], 200.0424 [M- 2 ^{i}Pr].

General Procedure for Cu complexes 2-4. Diethyl ether solutions (~ 3 mL) of CuBr·Me_2S and the appropriate tertiary phosphine were cooled to – 35 °C. The phosphine-containing solution was added to the CuBr·Me_2S suspension and the mixture was stirred and protected from the light with aluminum foil. After 5 minutes, a cooled (-35 °C) diethyl ether solution of **1** was added slowly to the reaction mixture, and the solution turned bright yellow immediately. After 2 hours of stirring the mixture was green-yellow, and the solvent was removed *in vacuo*. Extraction with benzene, followed by filtration through celite, yielded a bright yellow solution, which was lyophilized, affording spectroscopically pure product as a yellow powder.

[PN]Cu(PPh_3)$_2$ (2). X-Ray quality crystals were grown from vapor diffusion of a solution of **2** in diethyl ether with petroleum ether. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.3 (m, 30H, P(C_6H_5)$_3$), 7.02 (t, 2H, Ar-*H*), 6.92 (t, 3H, Ar-*H*), 6.79 (t, 1H, Ar-*H*), 6.72 (t, 1H, Ar-*H*), 6.59 (t, 1H, Ar-*H*), 6.17 (t, 1H, Ar-*H*), 2.26 (sept., 2H, C*H*(CH_3)$_2$), 1.08 (dd, 6H, CH(CH_3)$_2$), .99 (dd, 6H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz): δ 166.41, 158.39, 136.03 (d, J_{PC} = 12.6 Hz), 134.61 (d, J_{PC} = 16.9 Hz), 133.34, 132.43, 129.81, 129.76, 129.14 (d, J_{PC} = 8.3 Hz), 128.93, 126.05, 119.70, 113.40 (d, J_{PC} = 156 Hz), 23.85 (d, J_{PC} = 12.31 Hz), 20.22 (d, J_{PC} = 10.87 Hz), 19.02 (d, J_{PC} = 3.0 Hz). ^{31}P NMR (120 MHz): δ -1.2 (br, 2P), -3.7 (br, 1P). Anal. calcd. for $C_{54}H_{53}CuNP_3$ C, 74.34; H, 6.12; N, 1.61; Found: C, 74.31; H, 5.94; N, 1.60.

[PN]Cu(PMe_3)$_2$ (3). X-Ray quality crystals were grown from a vapor diffusion of a diethyl ether solution of **3** with petroleum ether. ^{1}H NMR (C_6D_6, 300 MHz,): δ 7.72 (q, 1H, Ar-*H*), 7.4 (m, 2H, Ar-*H*), 7.29 (t, 2H, Ar-*H*), 7.2-7.0 (m, 2H, Ar-*H*), 6.78 (tt, 1H, Ar-*H*), 6.54 (t, 1H, Ar-*H*), 1.95 (sept., 2H, C*H*(CH_3)$_2$), 1.10 (q, 6H, CH(CH_3)$_2$), 1.00 (q, 6H, CH(CH_3)$_2$), 0.85 (br. 18H, P(CH_3)$_3$). ^{13}C NMR (125 MHz): δ 163.40, 158.20, 131.80, 130.65, 128.79, 128.19, 121.20, 117.63 (d, J_{PC} = 34.9 Hz), 114.95, 114.07 (dd, JPC = 478.5 Hz, 3.7 Hz), 22.45 (d, J_{PC} = 8.8 Hz), 19.63 (d, J_{PC} = 11.6 Hz), 18.41 (d, J_{PC} = 3.3 Hz), 16.63 (d, J_{PC} = 13.0 Hz). ^{31}P NMR (120 MHz): δ 7.0 (br, 1P, [*P*N]), -46.3 (br, 2P, *P*(CH_3)$_3$). Anal. calcd. for $C_{24}H_{41}CuNP_3$ C, 57.64; H, 8.26; N, 2.80; Found: C, 57.61; H, 8.00; N, 2.84.

[PN]CuDPPE (4). Crystals used for X-Ray diffraction were grown from vapor diffusion of petroleum ether and a solution of **4** in THF. ^{1}H NMR (C_6D_6, 300 Mhz,): δ 7.65 (q, 2H, Ar-*H*), 7.44 (m, 8H, DPPE), 7.2-7.1 (m, 2H, Ar-*H*), 7.02 (d, 12H, DPPE), 6.9 (m, 3H, Ar-*H*), 6.55 (m, 2H, Ar-*H*), 2.18 (t, 4H, DPPE), 2.08 (sept., 2H, C*H*(CH_3)$_2$), 1.15 (q, 6H, CH(CH_3)$_2$), 0.89 (q, 6H, CH(CH_3)$_2$). ^{13}C NMR (125 MHz): δ 159.27, 136.06, 133.82 (t, J_{PC} = 8.1 Hz), 133.18, 131.53, 129.26, 129.09 (t, J_{PC} = 4.3 Hz), 124.15, 117.03, 114.20 (dd, J_{PC} = 571.3 Hz, 4.7 Hz), 68.16 (THF), 27.36 (td J_{PC} = 17.1 Hz, 5.5 Hz), 26.16 (THF), 23.09 (d, J_{PC} = 11.9 Hz), 19.89 (d, J_{PC} = 11.1 Hz), 17.97. ^{31}P NMR (120 Mhz): δ 8.7 (br, 1P, [*P*N]), -1.4 (br 2P, DPPE). Anal. calcd. for $C_{44}H_{47}CuNP_3$ C, 70.81; H, 6.35; N, 1.88; Found: C, 70.52; H, 6.46; N, 1.60.

2-Fluoro-5-methyl-diphenylamine. In a glovebox, a 200 mL high-pressure reaction vessel was charged with 30 mL toluene, Pd_2dba_3 (91.7 mg, 0.10 mmol), and 2-(dicyclohexylphosphino)biphenyl (140.2 mg, 0.40 mmol). The reaction flask was then removed from the box and stirred, with the dark red mixture turning more orange. As the reaction flask was stirring, 2-Fluoro-5-methylaniline (3.01 g, 24.05 mmol), iodobenzene (4.09 g, 20.04 mmol), and dry toluene were added to a 50 mL Schlenk flask, which was then boil-degassed. After subsequent cannula transfer of the organics into the high-pressure vessel, NaO^{t}Bu (2.70 g, 28.05 mmol) was added under N_2 counterflow, and the flask was sealed with a Teflon stopper. The mixture was heated to 110 °C for 20 hours, was allowed to cool to room temperature, then was filtered through a plug of silica, washing with copious petroleum ether (~250 mL). The solvent was removed, yielding an orange-brown oil. The crude product was purified by column chromatography on silica gel with petroleum ether eluent, affording the title compound as a pale yellow oil (3.01 g, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31 (t, 2H), 7.12 (d, 3H), 7.00 (m, 2H), 6.64 (t, 1H), 6.75 (bs, 1H, N*H*), 2.27 (s, 3H, -CH_3). ^{19}F NMR (282 MHz): δ -137.59 (s, 1F). HRMS (EI$^+$) *m/z* calcd. for $C_{13}H_{12}FN$: 201.0954. Found: 201.0957 [M^+].

[^{Me}PN]Li (5).[5] A 10 mL THF solution of 2-fluoro-5-methyldiphenylamine (1.452 g, 5.19 mmol) was cooled to – 35 °C and added to a 100 mL high pressure flask. To this vessel was added a 1.6 *M* solution of *n*BuLi in hexanes (3.41 mL, 5.45 mmol), dropwise with stirring. The clear colorless solution turned yellow, then orange, as it was warmed to room temperature, after which it was stirred for 2 hours. A 10 mL THF solution of LiP(*i*Pr)$_2$ (1.611 g, 12.99 mmol) was added slowly to the mixture, and the vessel was sealed with a Teflon stopper, removed from the glovebox, and heated to 80 °C for 7 days. After this time, a GC-MS trace showed complete consumption of starting material and growth of one other peak corresponding to product. The flask was brought back into the glovebox, and the reaction was quenched with 5 mL EtOH, resulting in a pale green color, before removal of solvents. Filtration of the residue through silica, washing with copious petroleum ether, followed by removal of solvents in vacuo and another filtration through celite, yielded [^{Me}PN]Li as a mixture with another phosphorous-containing product (80% by 31P NMR integration). Addition of *n*BuLi (3.41 mL, 5.45 mmol) to a cooled (-35 °C) solution of this crude product in a solution of 10 mL petroleum ether resulted in immediate precipitation of beige solids. The mixture was stirred 2.5 hrs before collecting the solids on a frit, and washing with 60 mL petroleum ether, affording pure **5**. ^{1}H NMR (THF-d^8, 300 Mhz): δ 6.7-6.9 (m, 6H), 6.25 (t, 1H), 5.98 (d, 1H), 1.96-2.06 (m, 5H, Ar-CH_3, CH(CH_3)$_2$), 1.10 (dd, 6H), 0.95 (d, 6H). ^{31}P NMR (120 MHz): δ -7.07 (m, 1H). HRMS (EI$^+$) *m/z* calcd. for $C_{19}H_{26}NP$: 299.1805. Found: 299.1803 [M^+], 257.1387 [M-^{i}Pr], 214.0860 [M- 2 ^{i}Pr].

2-Fluoro-5-trifluormethyl-diphenylamine. In the glovebox, a 200 mL Teflon-stopped reaction vessel was charged with Pd_2dba_3 (44.9 mg, 0.049 mmol), 2-(dicyclohexylphosphino)biphenyl (68.7 mg, 0.196 mmol), NaOtBu (1.32 g, 13.7 mmol), and 15 mL toluene. This vessel was removed from the box, and stirred for 10 minutes, wherein the dark red mixture took on a more orange appearance. Under a purge of N_2, 1-Fluoro-4-trifluoromethyl-aniline (1.53 mL, 11.76 mmol) and iodobenzene (1.09 mL, 9.8 mmol) were added to the vessel by syringe. The mixture was then sealed with the Teflon

stopper, and heated to 100 °C in an oil bath overnight. After 18 hours, the reaction was shown to be complete by GC-MS, at which point the mixture was filtered through a large plug of silica, and washed with copious (~200 mL) petroleum ether, yielding a pale orange solution. The solvents were removed by rotary evaporation, yielding an orange oil. Upon storage at -30 °C overnight, crystalline orange needles of pure compound were obtained (1.939 g, 78%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53 (dd, 1H), 7.4-7.33 (m, 2H), 7.2-7.05 (m, 4H), 5.82 (br N*H*). ^{19}F NMR (282 MHz): δ -58.8 (3F), -125.5 (1F). HRMS (FAB^+) *m/z* calcd. for $C_{13}H_9F_4N$: 255.0671. Found: 255.0682 [M^+].

[^{CF3}PN]Li (6).[5] In the glovebox, 1-Fluoro-4-trifluoromethyl-diphenylamine (1.94 g, 7.63 mmol) was dissolved in 20 mL THF, and added to a 200 mL Teflon-stopped glass vessel equipped with a stirbar. The vessel was cooled to -78 °C, at which point a 1.6 *M* hexanes solution of *n*BuLi (4.8 mL, 7.71 mmol) was added dropwise by syringe. The reaction mixture was allowed to warm with stirring for 30 minutes, during which time the solution darkened from pale orange to a darker orange-brown. At this point a 10 mL THF solution of LiP(*i*Pr)$_2$ (1.90 g, 15.33 mmol) was added to the reaction mixture, and the vessel was heated to 70 °C for 4 days, while monitoring the reaction for completion by GC-MS and ^{31}P NMR. The reaction mixture, which had darkened to a red-brown, was luminescent yellow under a UV lamp. The vessel was cooled to room temperature, and was brought into the glovebox. The mixture was then quenched with 10 mL EtOH, and 10 mL of petroleum ether were added, yielding a golden-brown solution. The solvents were removed *in vacuo*. The oily residue was treated with 10 mL of diethyl ether, which was subsequently removed under reduced pressure; this procedure was repeated as necessary to reduce bubbling. The residue was extracted with petroleum ether, filtered through celite, and concentrated to a brown oil, which was left under dynamic vacuum overnight. The residue contained a mixture of [^{CF3}PN]H (~85-90%) and one unknown P-containing side-product (δ +4 ppm). Crude [^{CF3}PN]H was dissolved in 20 mL of petroleum ether, added to a 100 mL round-bottom flask, and cooled to -35 °C. A 1.6 *M* hexanes solution of *n*BuLi (4.8 mL, 7.71 mmol) was then added dropwise by syringe, yielding a beige precipitate. The flask was warmed to room temperature and stirred overnight, at which point the solids were collected on a sintered glass frit, and washed with 40 mL petroleum ether, yielding spectroscopically pure **6** (1.61 g, 59%). ^{1}H NMR (THF-d^8, 300 MHz): δ 7.15 (d, 1H), 7.05-6.94 (m, 3H), 6.82 (dd, 2H), 6.45 (t, 1H), 6.24 (dd, 2H), 2.09 (sept, 2H, C*H*(CH$_3$)$_2$), 1.14 (q, 6H, CH(C*H*$_3$)$_2$), 1.00 (q, 6H, CH(C*H*$_3$)$_2$). ^{31}P NMR: δ -6.6 (br q, 1P). ^{19}F NMR: δ -60.5 (s, 3F). HRMS (EI^+) *m/z* calcd. for $C_{19}H_{23}F_3NP$: 353.1520. Found: 353.1506 [M^+], 311.1105 [M - ^{i}Pr], 268.0594 [M - 2 ^{i}Pr], 235.0692 [M-(^{i}Pr)$_2$P].

[MePN]Cu(PPh$_3$)$_2$ (7). Diethyl ether solutions of **5** (67.7 mg, 0.222 mmol), CuBr·Me$_2$S (45.6 mg, 0.222 mmol), and PPh_3 (116.3 mg, 0.444 mmol) were cooled to – 35 °C. PPh_3 was added to the cold suspension of CuBr·Me$_2$S with stirring, and the scintillation vial was covered with aluminum foil. After 5 minutes amide **5** was added slowly, and the reaction mixture was stirred for 2.5 hrs. After removal of solvent in vacuo, the residue was extracted with benzene, filtered through celite, and lyophilized, yielding **7** in quantitative yield as a yellow powder. X-Ray quality crystals were grown from a diethyl ether solution of **7** layered with petroleum ether and cooled to -30 °C. ^{1}H NMR (C_6H_6, 300 MHz): δ 7.48-7.35 (m, 12H, P(C$_6$*H*$_5$)$_3$), 7.26 (d, Ar-*H*), 7.2-7.1 (m), 7.08-7.0 (m,

18H, P(C_6H_5)$_3$), 6.86 (t, 1H, Ar-*H*), 6.42 (d, 1H, Ar-*H*), 2.11 (s, 3H, [C*H*3PN]), 2.06 (sept, 2H, C*H*(CH_3)$_2$), 1.1-0.94 (m, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz): δ 166.54, 158.34, 141.69, 135.80 (d, J_{PC} = 12.0 Hz), 134.18 (d, J_{PC} = 17.2 Hz), 132.98, 129.51, 128.87 (d, J_{PC} = 8.3 Hz), 125.88, 119.35, 114.05 (dd, J_{PC} = 75.3 Hz, 4.9 Hz), 23.51 (d, J_{PC} = 13.1 Hz), 22.15, 19.92 (d, J_{PC} = 11.2 Hz), 18.67 (d, J_{PC} = 3.7 Hz). ^{31}P NMR (120 MHz): δ 1.1 (2P), -3.9 (1P). Anal. calcd. for $C_{55}H_{55}CuNP_3$ C, 74.52; H, 6.25; N, 1.58. Found: C, 74.42; H, 6.45; N, 1.57.

[^{CF3}PN]Cu(PPh$_3$)$_2$ (8). Diethyl ether solutions of **6** (97.8 mg, .273 mmol), CuBr·Me_2S (56.0 mg, .273 mmol), and PPh_3 (142.9 mg, .545 mmol) were cooled in scintillation vials to -35 °C. The PPh_3 solution was added to the slurry of CuBr·Me_2S, before the vial was covered with aluminum foil and stirred for 5 minutes. Amide **6** was slowly added to the slurry via pipette, which immediately resulted in a clear yellow solution. The reaction was stirred 2 hr, at which point the solvents were removed *in vacuo*. The residues were extracted with benzene, and filtered through celite, yielding a bright yellow solution. The benzene was removed by lyophilization overnight, affording spectroscopically pure yellow powder (254.6 mg, 99%). X-Ray quality crystals were grown from a cooled (-30 C) layering of petroleum ether upon a diethyl ether solution of **8**. ^{1}H NMR (C_6D_6, 300 Mhz): δ 7.65 (d, 1H, [PN]Ar-*H*), 7.4 (m, 12H, P(C_6H_5)$_3$), 7.29 (d, 2H, [PN]Ar-*H*), 7.08 (t, 3H, [PN]Ar-*H*), 7.0 (m, 18 H, P(C_6H_5)$_3$), 6.83 (t, 1H, [PN]Ar-*H*), 6.76 (d, 1H, [PN]Ar-*H*), 1.933 (sept., 2H, C*H*(CH_3)$_2$), 0.977 (dd, 6H, CH(C*H*$_3$)$_2$), 0.873 (dd, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (125 MHz): δ 135.64 (d, J_{PC} = 15.6 Hz), 134.54 (d, J_{PC} = 17.09), 133.35, 129.59, 129.97 (d, J_{PC} = 0.9 Hz), 129.20 (d, J_{PC} = 8.3 Hz), 128.92 (d, J_{PC} = 0.4 Hz), 125.42, 120.57, 109.41, 106.95, 23.86 (d, J_{PC} = 12.4 Hz), 20.11 (d, J_{PC} = 11.1 Hz), 18.91 (d, J_{PC} = 3.1 Hz). ^{31}P NMR (120 MHz): δ 0.19 (br, 2P, *P*(C_6H_5)$_3$), -3.98 (br, 1P, [*P*N]). 19 F NMR (470 MHz): -63.4 (3F). Anal. calcd. for $C_{55}H_{52}CuF_3NP_3$ C, 70.24; H, 5.57; N, 1.49. Found: C, 70.10; H, 5.84; N, 1.45.

[PN]Ag(PPh$_3$)$_2$ (9). A 20 mL scintillation vial protected from the light was charged with AgOTf and 3 mL diethyl ether. To the stirring solution was added a diethyl ether solution of PPh_3, and five minutes subsequently was added a solution of **1**. After 2 hours, the reaction mixture was filtered, and the bright yellow solution was dried *in vacuo*. Analytically pure crystals were grown from a THF solution layered with petroleum ethers, and cooled to -30 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.71 (t, 1H, Ar-*H*), 7.49 (d, 2H, Ar-*H*), 7.38 (m, 12H, P(C_6H_5)$_3$), 7.2-7.1 (m, 4H, Ar-*H*), 7.05 (m, 18H, P(C_6H_5)$_3$), 6.77 (t, 1H, Ar-*H*), 6.55 (t, 1H, Ar-*H*), 2.02 (sept., 2H, C*H*(CH_3)$_2$), 1.08 (q, 6H, CH(C*H*$_3$)$_2$), 0.93 (q, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz): δ 159.2, 135.49 (d, J_{PC} = 12.9 Hz), 134.70 (d, J_{PC} = 17.5 Hz), 133.58, 131.82, 130.02, 129.70, 129.24 (d, J_{PC} = 8.59 Hz), 123.67, 116.88, 113.43 (d, J_{PC} = 33.2 Hz), 114.04 (d, J_{PC} = 342.2 Hz), 23.92 (d, J_{PC} = 7.44 Hz), 20.48 (d, J_{PC} = 12.31), 19.23 (d, J_{PC} = 4.87 Hz). ^{31}P NMR (120 MHz): δ 7.7 (1P), 5.5 (2P). Anal. Calcd. for $C_{54}H_{53}AgNP_3$ C, 70.74; H, 5.83; N, 1.53. Found: C, 70.67; H, 6.03; N, 1.51.

[PN]$_2$Zn (10). To a THF solution of $ZnCl_2$ (16.0 mg, .1174 mmol in 3 mL) chilled to -35 °C in a scintillation vial, was added 2 equivalents of **1** (68.4 mg, 0.235 mmol) in 5 mL cold THF solution, while stirring. The mixture was allowed to warm to room temperature

while stirring for 3 hours. The golden reaction solution was then filtered through celite, dried by evaporation, and extracted with diethyl ether. Filtration through celite, followed by washing with 2 mL ether, yielded a golden yellow solution that was layered with petroleum ether and cooled to -30 °C, affording golden crystals of analytically pure **10**. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.2-7.1 (m, 4H), 7.08-6.9 (m, 10H), 6.61 (t, 2H), 6.25 (m, 2H), 2.36 (sept, 4H, C*H*(CH_3)$_2$), 1.28 (q, 6H, CH(C*H*$_3$)$_2$), 1.18 (q, 6H, CH(C*H*$_3$)$_2$), 1.02 (q, 6H, CH(C*H*$_3$)$_2$), 0.36 (q, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR: δ 162.87 (t, J_{PC} = 7.8 Hz), 154.62, 132.77 (d, J_{PC} = 6.4 Hz), 129.87, 124.62, 120.69, 115.14, 113.26, 107.85 (t, J_{PC} = 21.2 Hz), 23.46 (t, J_{PC} = 7.4 Hz), 21.19 (t, J_{PC} = 10.5 Hz), 19.35 (t, J_{PC} = 3.6 Hz), 18.86 (t, J_{PC} = 4.1 Hz), 17.96 (t, br), 16.69 (s, br). ^{31}P NMR (120 MHz): δ -12.23 (2P). Anal calcd. for $C_{36}H_{46}ZnN_2P_2$ C, 68.19; H, 7.31; N, 4.42**.** Found: C, 68.47; H, 7.50; N, 4.04.

Table 4. Assorted photophysical properties of all reported complexes.

		λ_{em} (nm)				
Compound	**λ_{abs} (nm)**	**C_6H_6**	**Et_2O**	**THF**	**Stokes Shift, Solvent (nm)**	**λ (cm^{-1})[a]**
1	411, 354, 298	--	480	--	69, Et_2O	8970
2	434, 339	504	500	504	70, C_6H_6	2810
3	427, 350	497	495	501	70, C_6H_6	3080
4	423, 365	534	530	555	111, C_6H_6	7400
5	407, 355	--	465	--	58, Et_2O	4930
6	421, 354	--	550	--	129, Et_2O	6470
7	433, 342	498	499	506	65, C_6H_6	3000
8	444, 332	552	546	563	108, C_6H_6	5120
9	431, 353	544	--	--	113, C_6H_6	12460
10	394, 326	473	--	--	79, C_6H_6	5270

a. The reorganization energy $\lambda = (\Delta\nu_{1/2})^2 / (16RT \ln 2)$.
$\Delta\nu_{1/2}$ = Full width at half max.
R = 8.31451 J/mol·K
T = 298 K

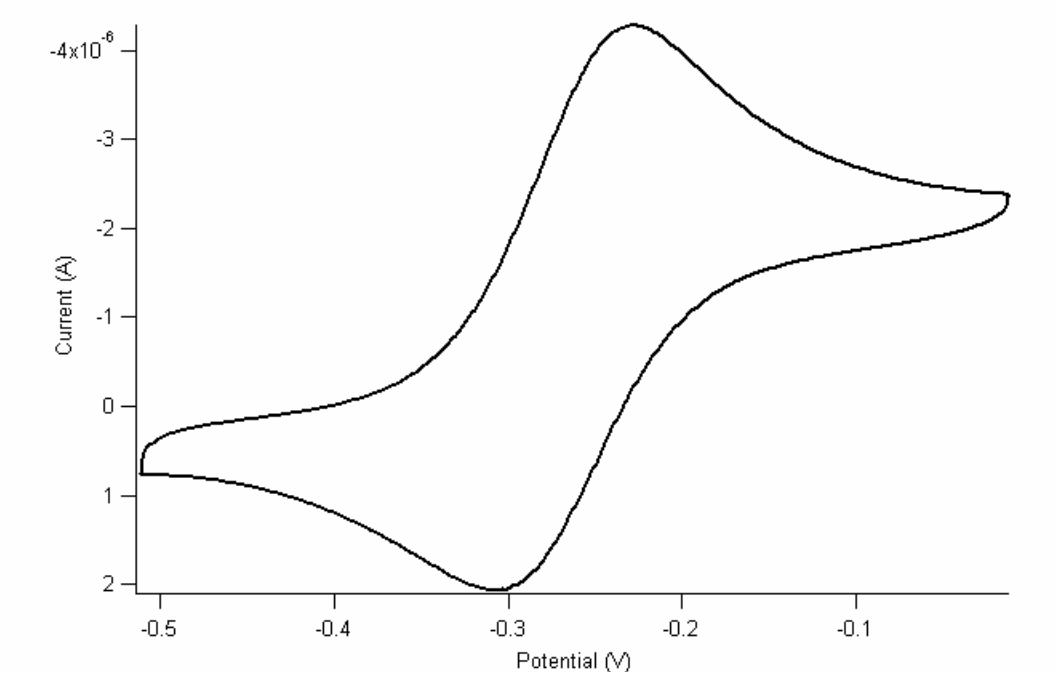

Figure S2. CV of $PNCu(PPh_3)_2$ (**2**)

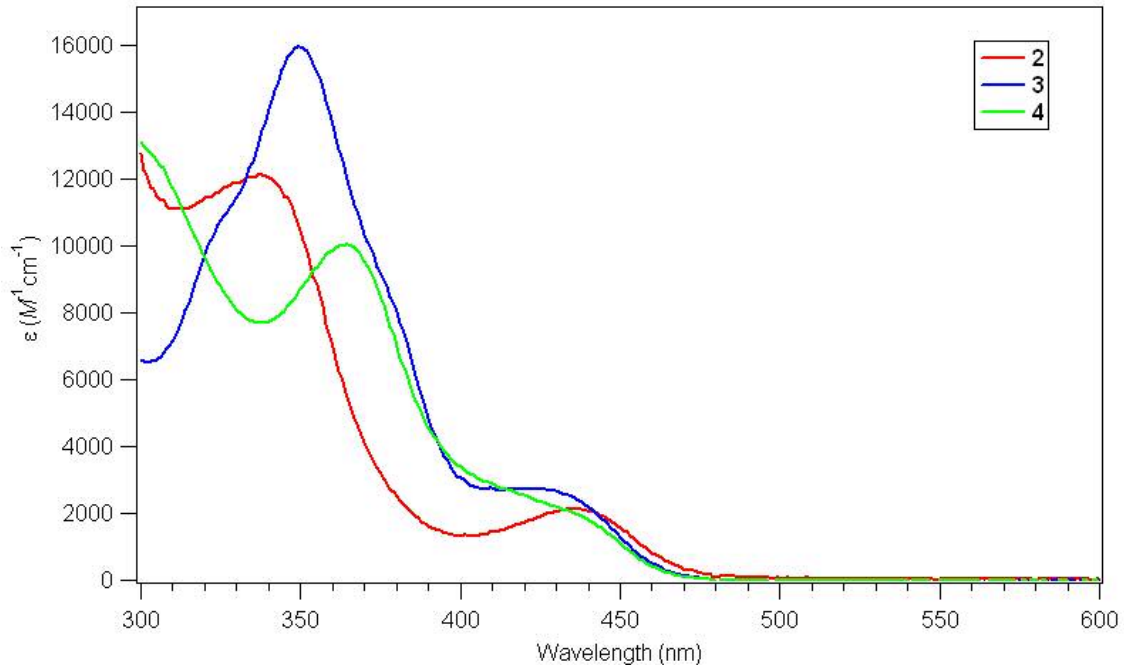

Figure S3. Overlay of Absorption Spectra of $PNCu(L)_2$ (L = PPh_3 (**2**), PMe_3 (**3**); $(L)_2$ = dppe (**4**).

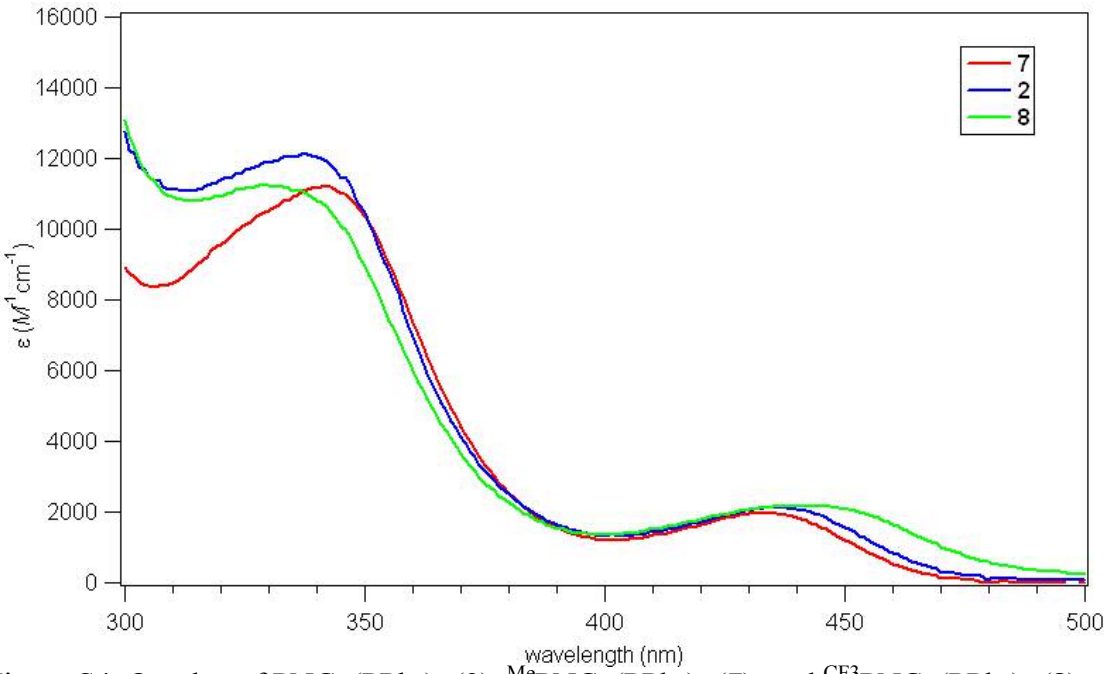

Figure S4. Overlay of $PNCu(PPh_3)_2$ (**2**), $^{Me}PNCu(PPh_3)_2$ (**7**), and $^{CF3}PNCu(PPh_3)_2$ (**8**).

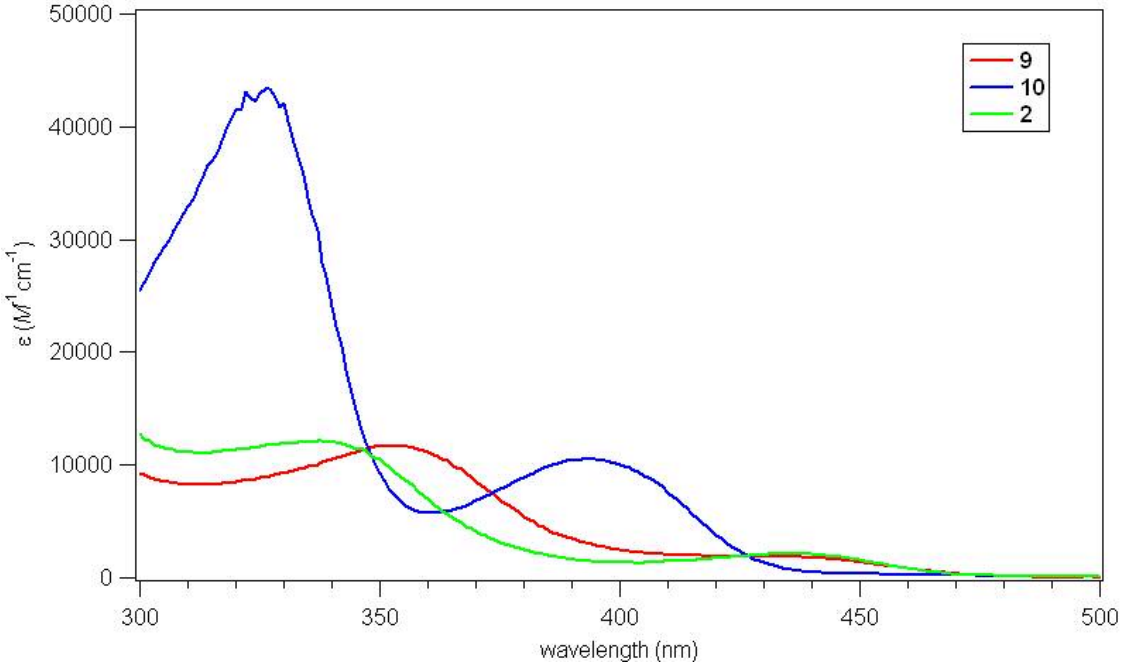

Figure S5. Overlay of $PNAg(PPh_3)_2$ (**9**), PN_2Zn (**10**), $PNCu(PPh_3)_2$ (**2**)

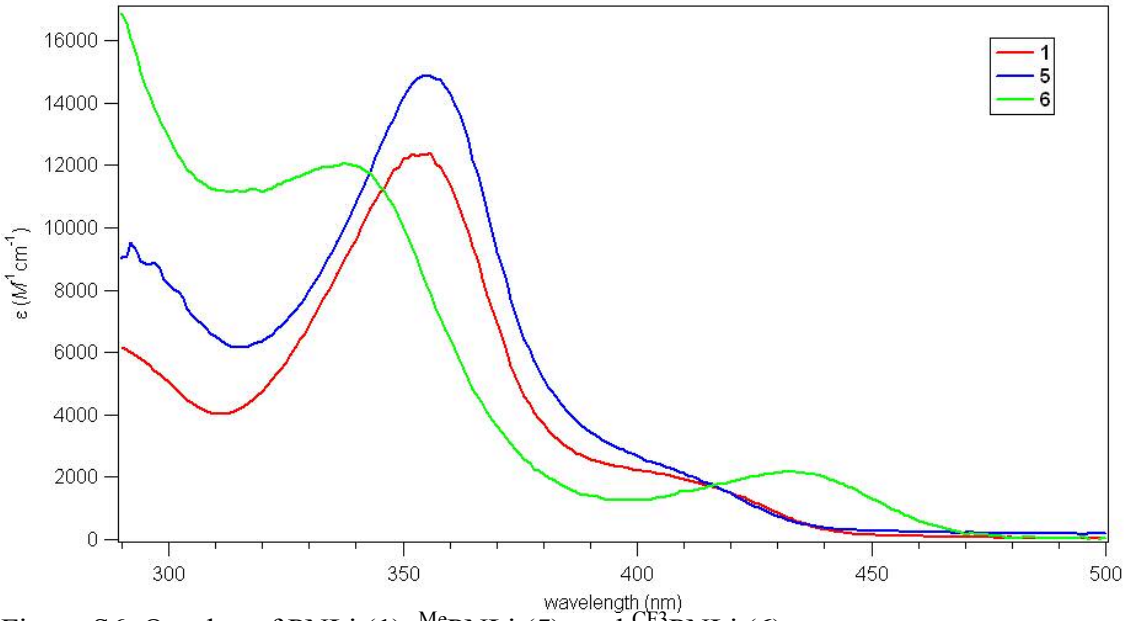

Figure S6. Overlay of PNLi (**1**), ^{Me}PNLi (**5**), and ^{CF3}PNLi (**6**).

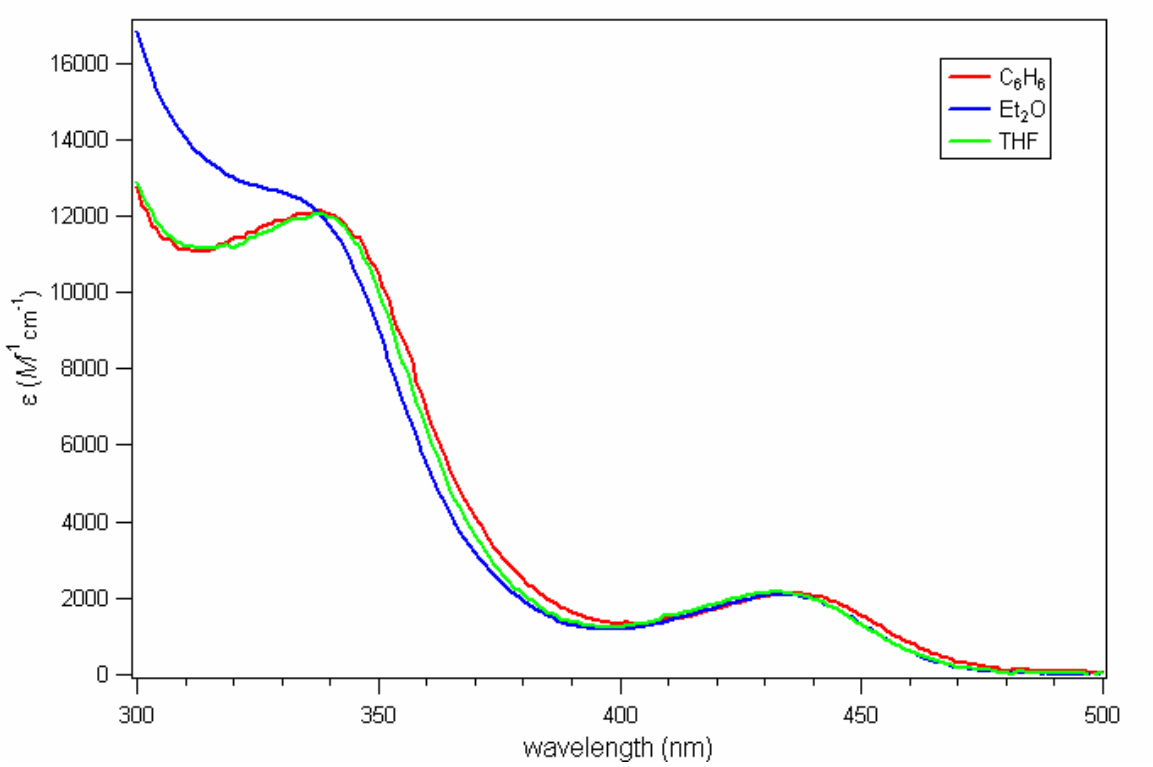

Figure S7. Optical Spectrum of $PNCu(PPh_3)_2$ (**2**) in Benzene, Diethyl Ether, and THF.

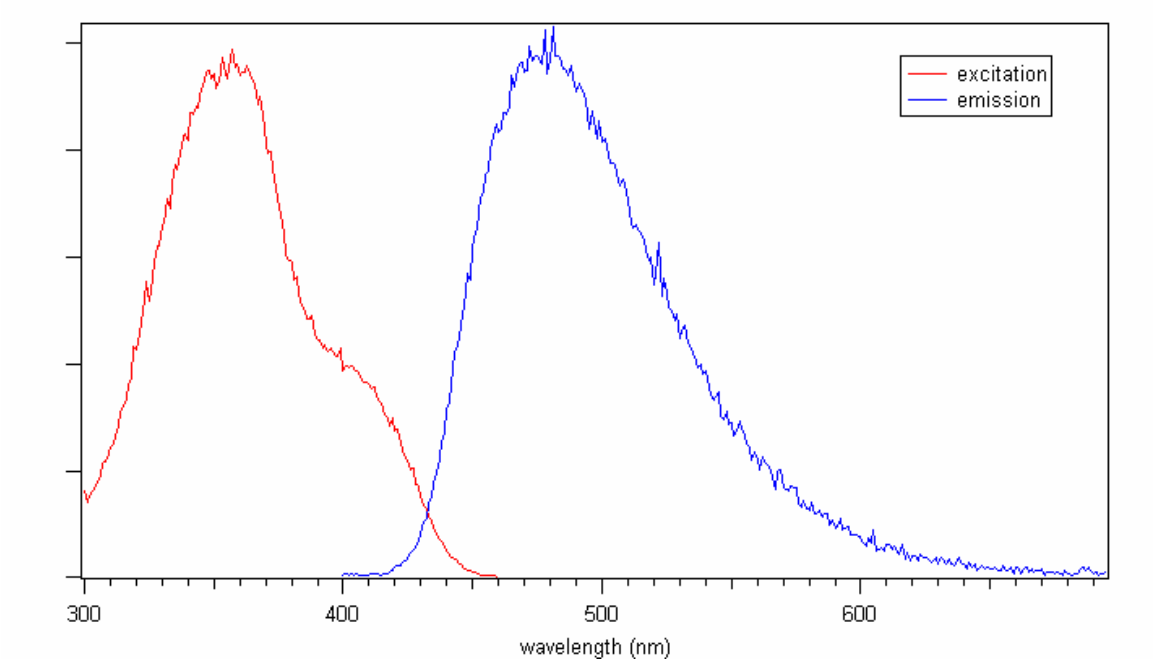

Figure S8. Emission/Excitation Spectra of [PN]Li (**1**; λ_{ex} = 350 nm).

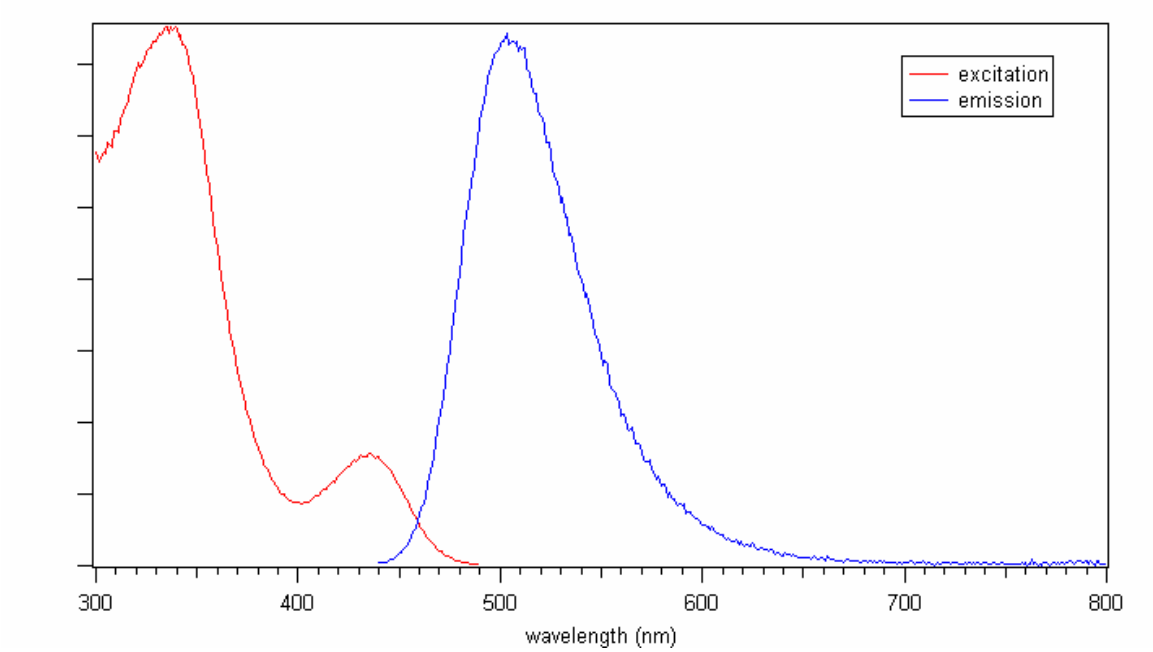

Figure S9. Emission/Excitation spectra of PNCu(PPh_3)$_2$ (**2**; λ_{ex} = 430 nm).

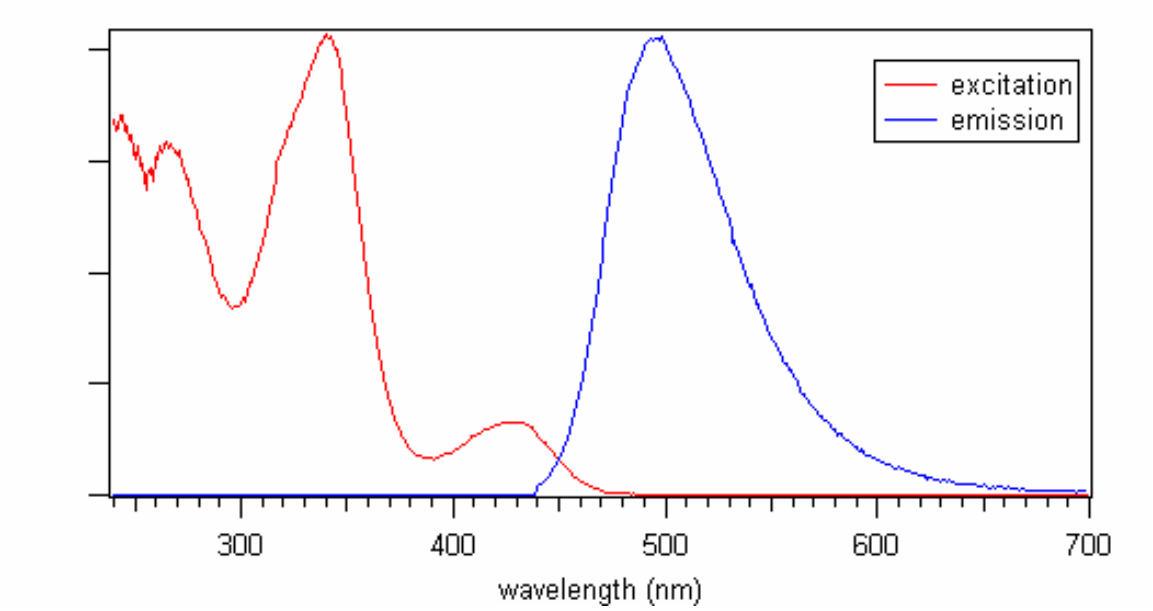

Figure S10. Emission/Excitation spectra of PNCu(PMe_3)$_2$ (**3**; λ_{ex} = 430 nm).

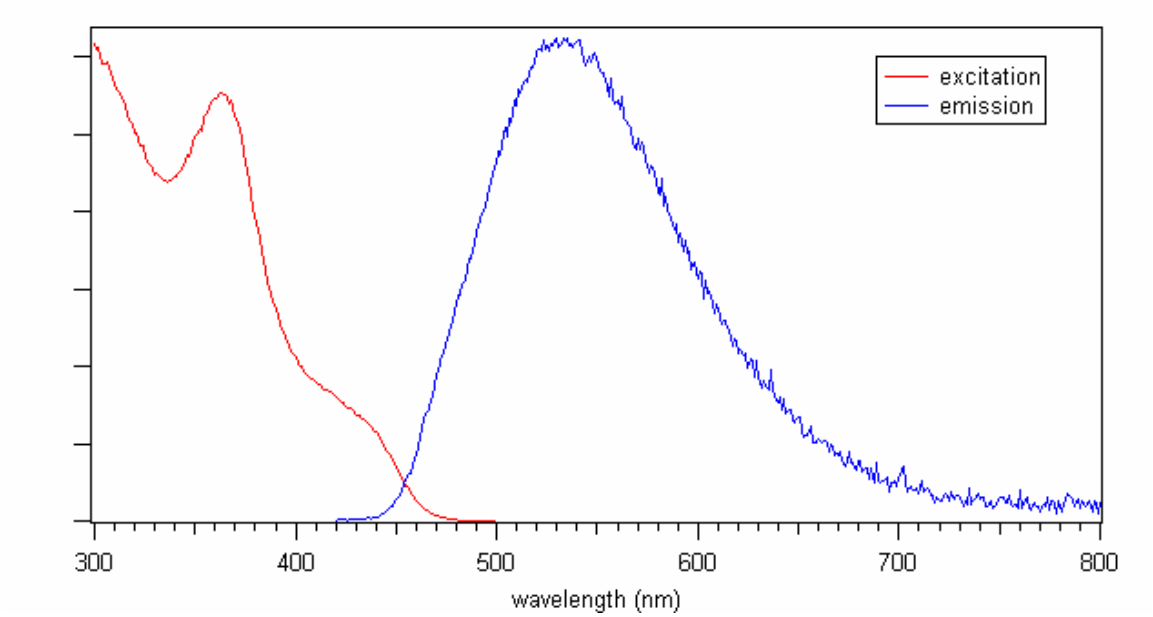

Figure S11. Emission/Excitation spectra of PNCudppe (**4**; λ_{ex} = 430 nm).

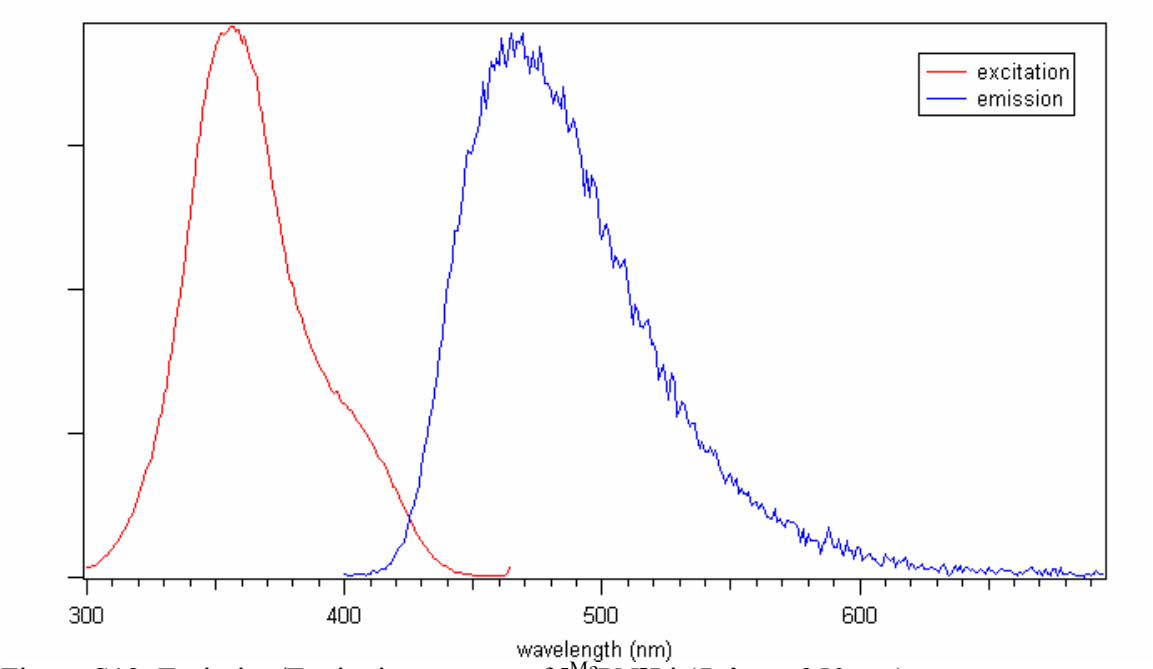

Figure S12. Emission/Excitation spectra of [^{Me}PN]Li (**5**; λ_{ex} = 350 nm)

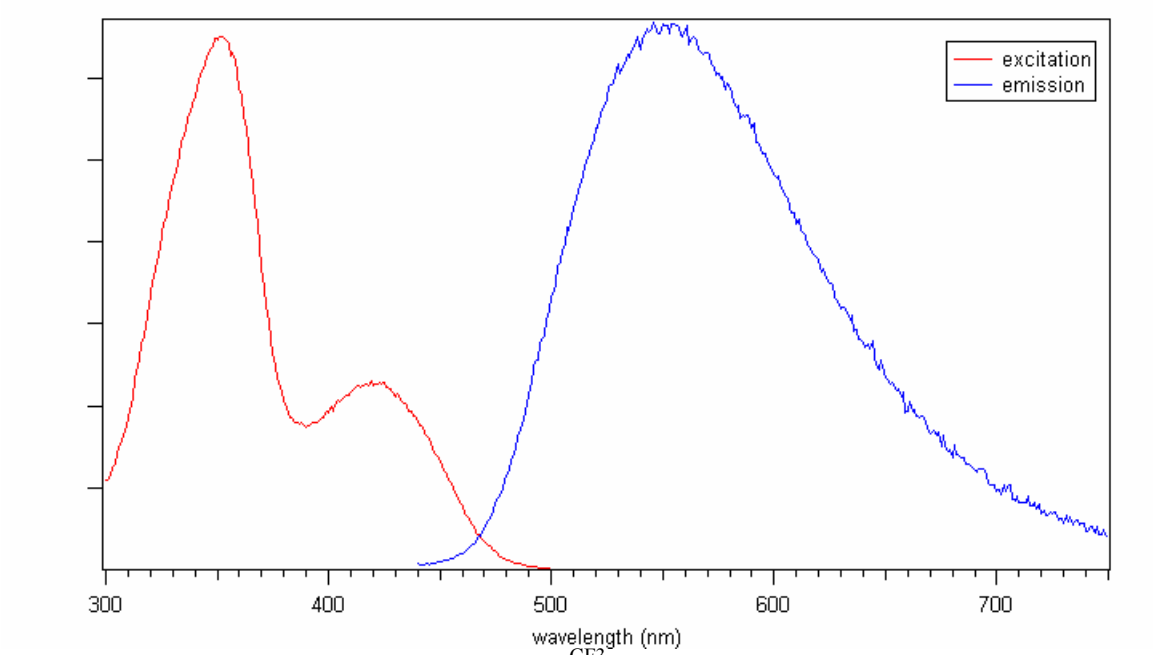

Figure S13. Emission/Excitation spectra of [^{CF3}PN]Li (**6**; λ_{ex} = 350 nm)

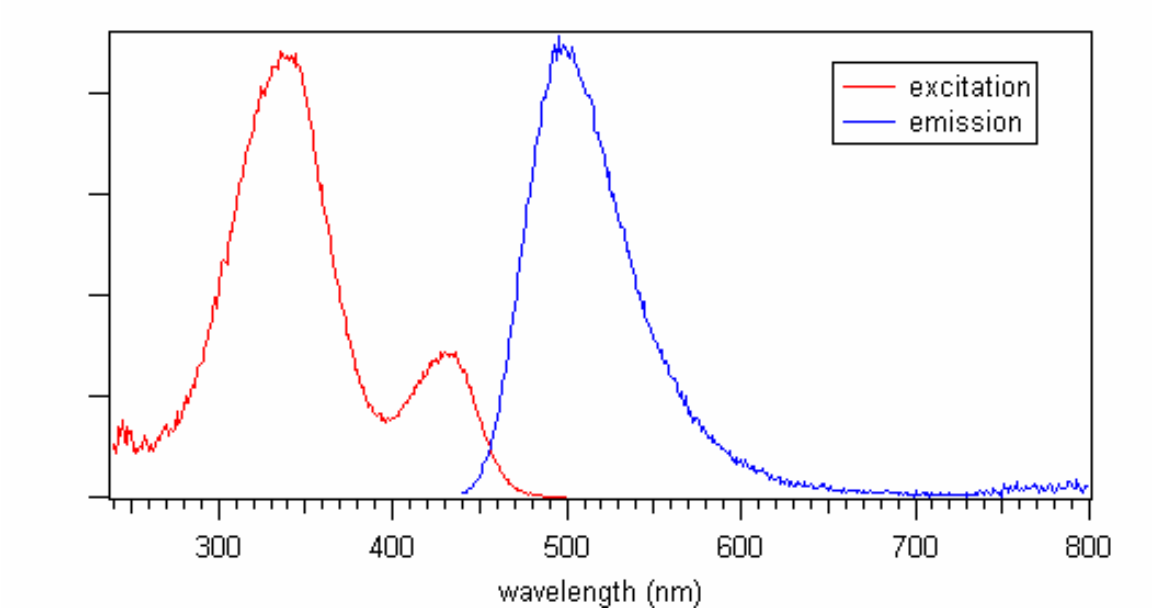

Figure S14. Emission/Excitation spectra of $MePNCu(PPh_3)_2$ (**7**; λ_{ex} = 430 nm).

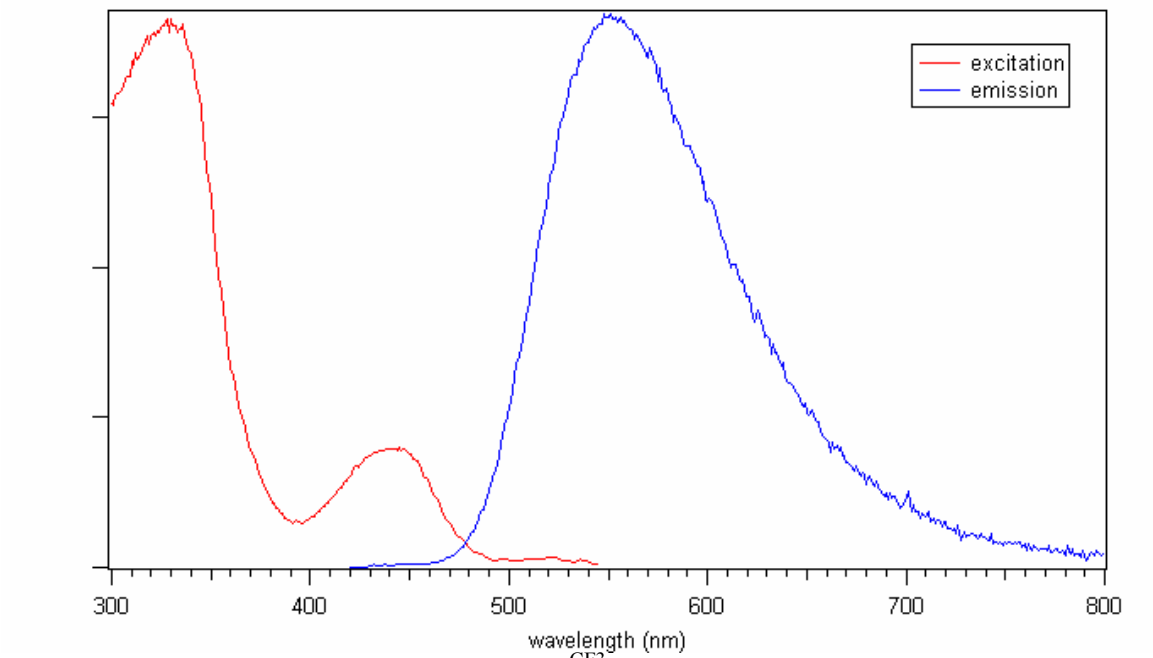

Figure S15. Emission/Excitation spectra of $[^{CF3}PN]Cu(PPh_3)_2$ (**8**; λ_{ex} = 430 nm).

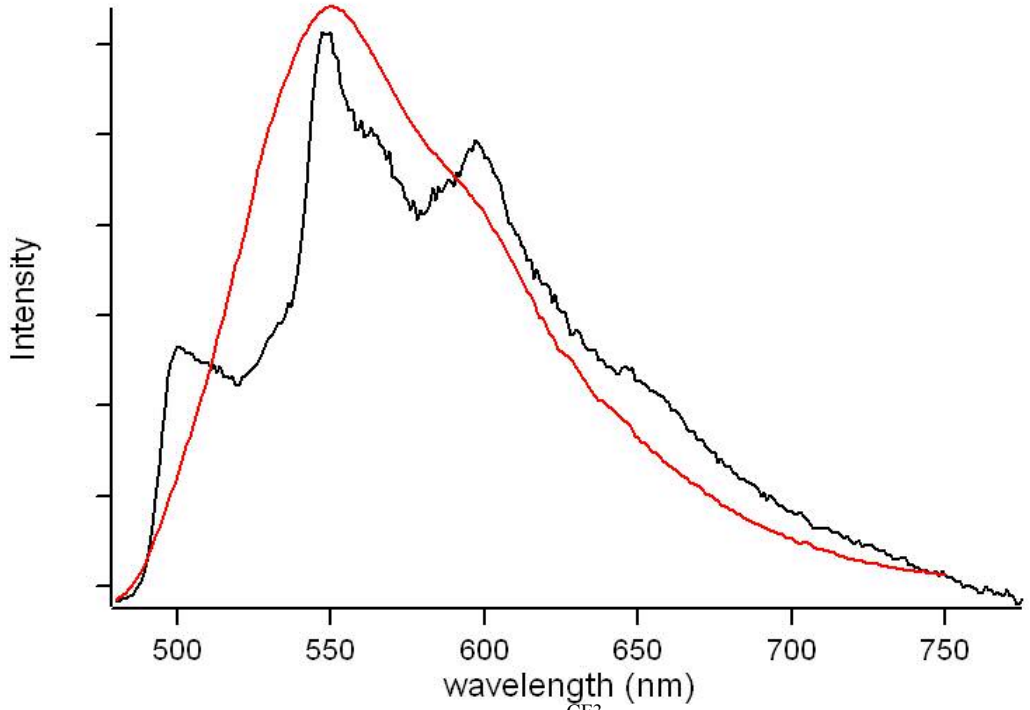

Figure S16. Emission spectra of polycrystalline [^{CF3}PN]Cu(PPh_3)$_2$ (**8**; λ_{ex} = 430 nm) at 77 K (black) and 298 K (red).

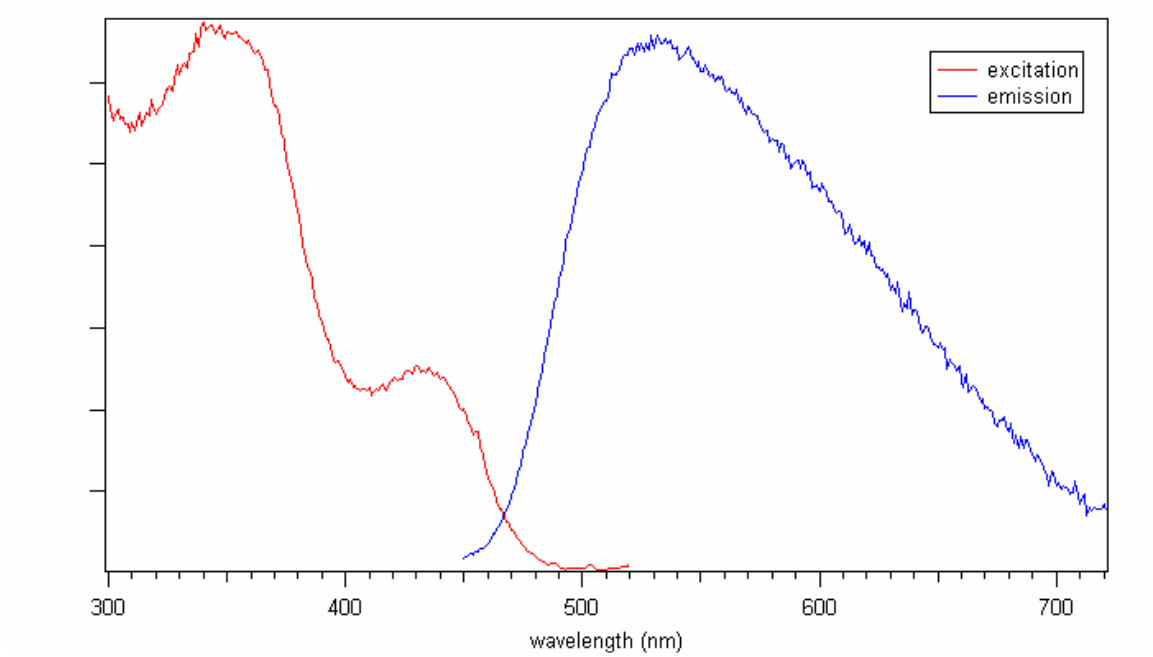

Figure S17. Emission/Excitation Spectra of PNAg(PPh_3)$_2$ (**9**; λ_{ex} = 430 nm).

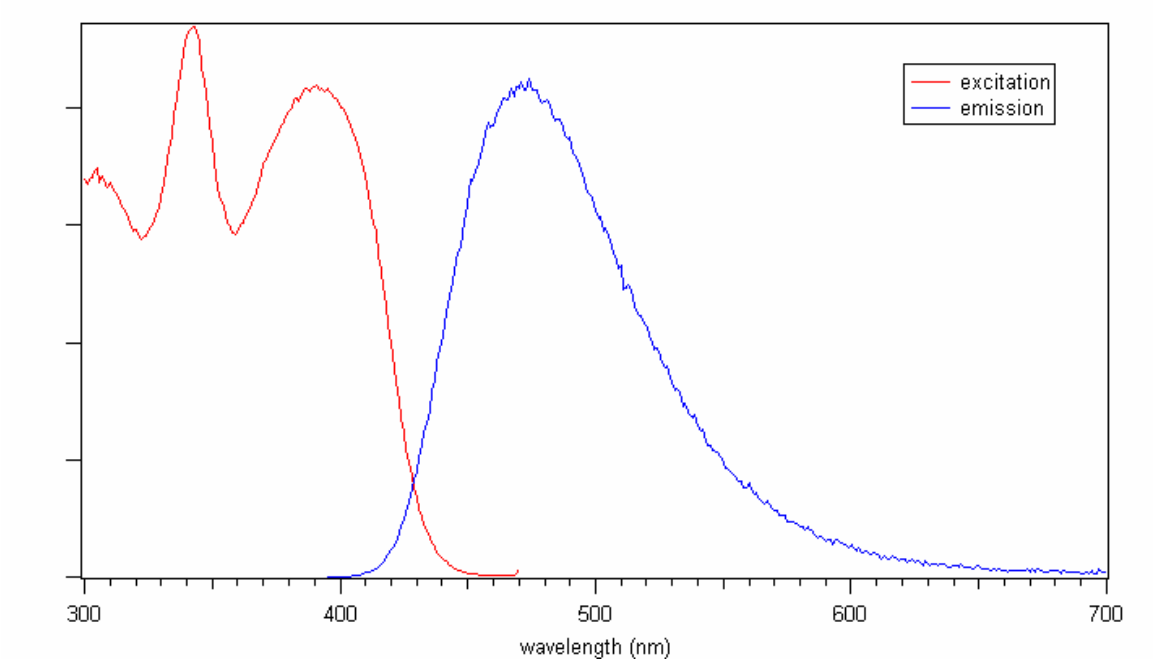

Figure S18. Emission/Excitation Spectra of PN_2Zn (**10**; λ_{ex} = 350 nm).

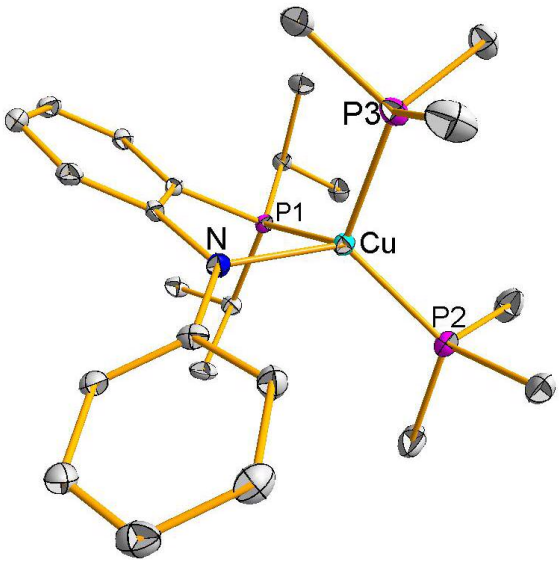

Figure S19. Structure of **3.** Key bond lengths (Å) and angles (°): Cu-N 2.086(1), Cu-P1 2.2744(5), Cu-P2 2.331(5), Cu-P3 2.2690(5), N-Cu-P1 82.54(4).

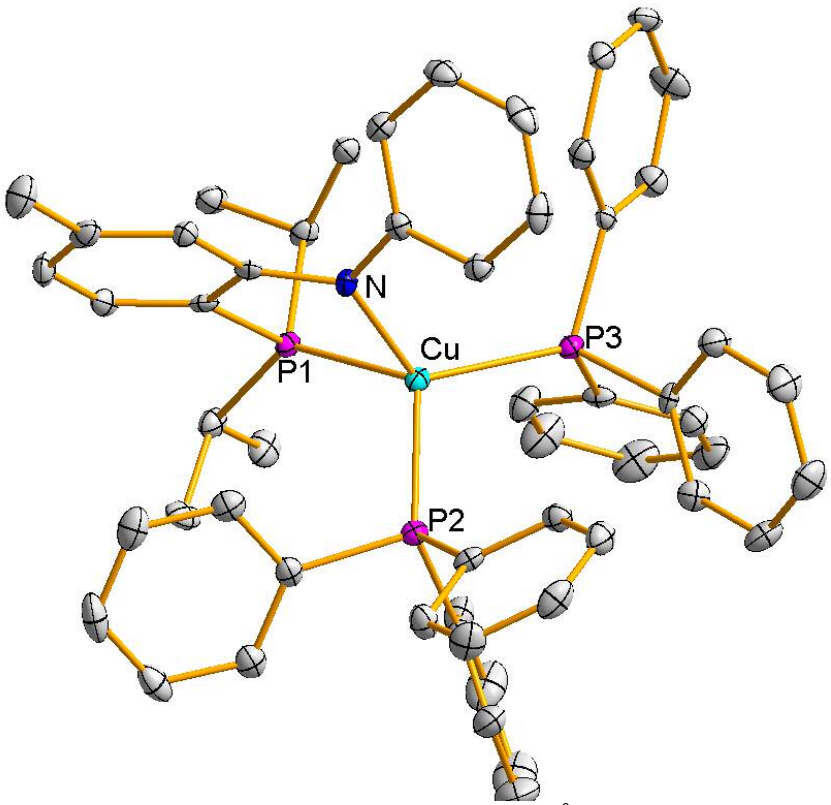

Figure S20. Structure of **7.** Key bond lengths (Å) and angles (°): Cu-N 2.076(2), Cu-P1 2.326(1), Cu-P2 2.3439(9), Cu-P3 2.3189(9), N-Cu-P1 82.24(7).

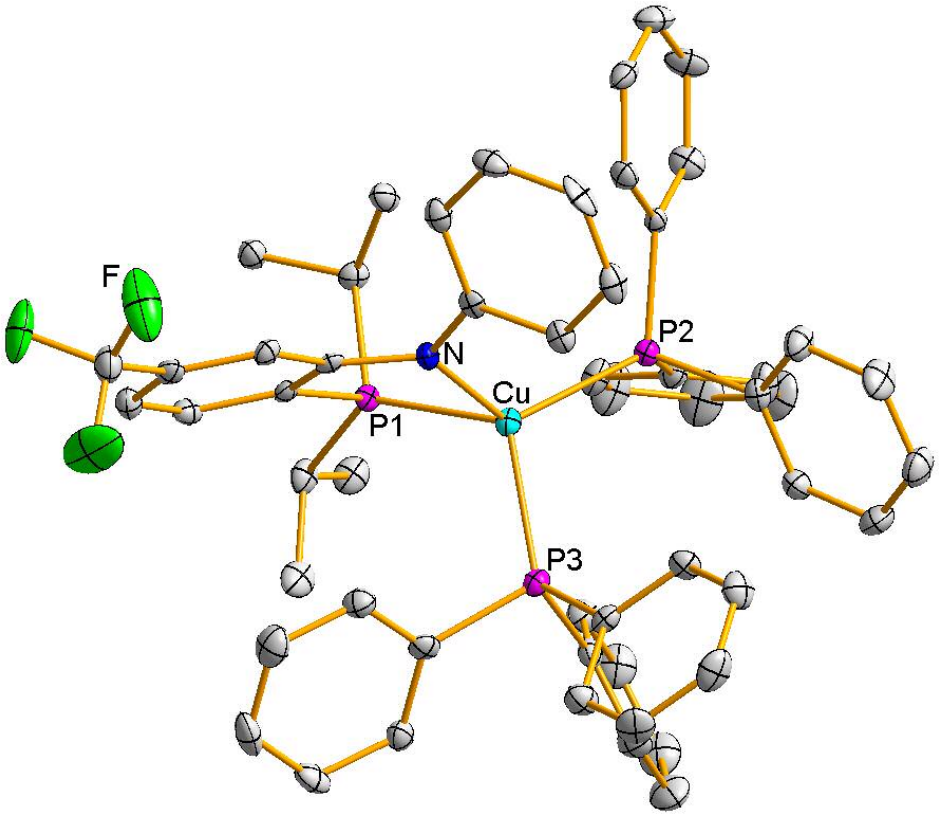

Figure S21. Structure of **8.** Key bond lengths (Å) and angles (°): Cu-N 2.091(4), Cu-P1 2.347(3), Cu-P2 2.329(3), Cu-P3 2.363(3), N-Cu-P1 82.1(2).

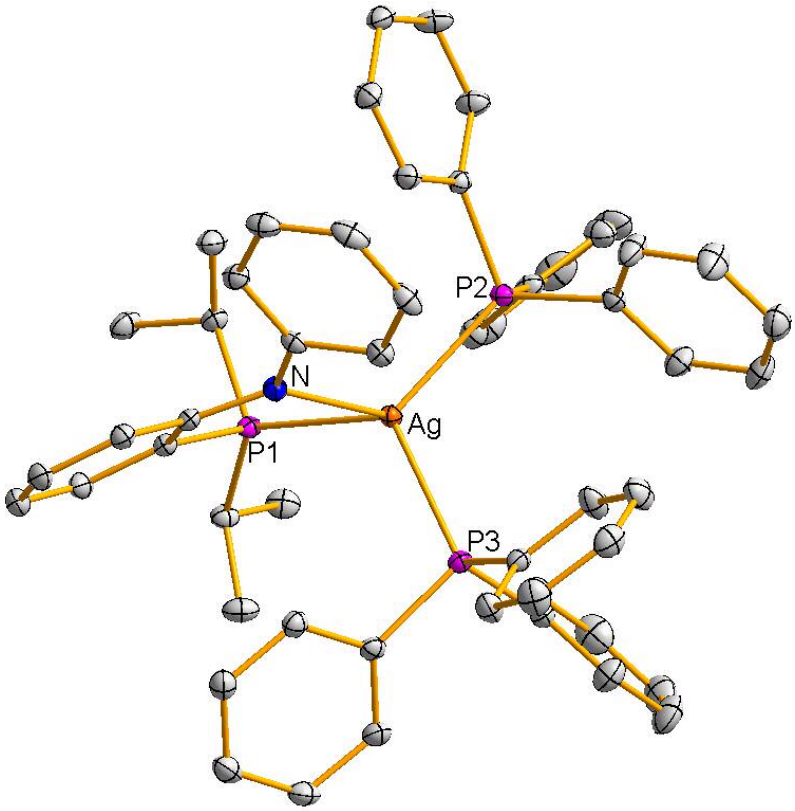

Figure S22. Structure of **9**. Key bond lengths (Å) and angles (°): Ag-N 2.369(1), Ag-P1 2.4881(4), Ag-P2 2.4919(4), Ag-P3 2.5028(4), N-Ag-P1 76.40(3).

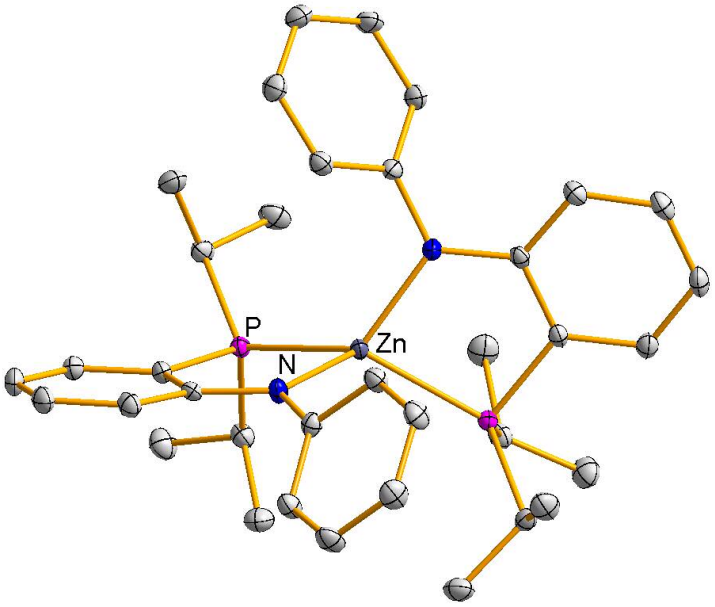

Figure S23. Structure of **10**. Key bond lengths (Å) and angles (°): Zn-N 1.969(2), Zn-P 2.372(1), N-Zn-P 85.72(4).

Crystallography.

Special Refinement Details.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles, and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

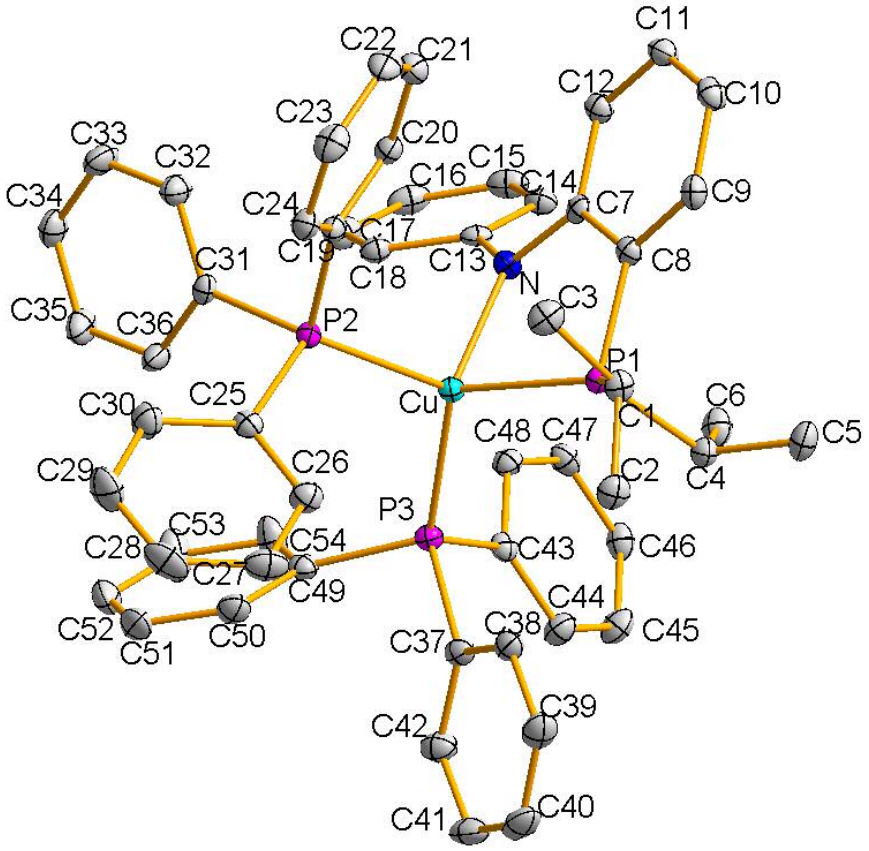

Figure S24. Fully numbered molecular structure of **2**. Hydrogen atoms omitted for clarity.

$PNCu(PPh_3)_2$ (**2**)

Table 1. Crystal data and structure refinement for $PNCu(PPh_3)_2$ (**2**).

Identification code	$PNCu(PPh_3)_2$	
Empirical formula	C54 H53 Cu N P3	
Formula weight	872.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.764(2) Å	α= 90°.
	b = 18.894(4) Å	β= 98.135(13)°.
	c = 22.199(4) Å	γ = 90°.
Volume	4469.0(14) $Å^3$	
Z	4	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.634 mm^{-1}	
F(000)	1832	
Crystal size	0.407 x 0.241 x 0.222 mm^3	
Theta range for data collection	1.85 to 36.01°.	
Index ranges	-16≤h≤17, -30≤k≤24, -36≤l≤32	

Reflections collected	73459
Independent reflections	18249 [R(int) = 0.0805]
Completeness to theta = 36.01°	86.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18249 / 0 / 536
Goodness-of-fit on F^2	1.309
Final R indices [I>2σ(I)]	R1 = 0.0469, wR2 = 0.0704
R indices (all data)	R1 = 0.0878, wR2 = 0.0757
Largest diff. peak and hole	1.560 and -0.852 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $PNCu(PPh_3)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	6584(1)	2629(1)	5930(1)	12(1)
P(2)	7325(1)	1788(1)	6662(1)	13(1)
P(1)	8081(1)	3309(1)	5545(1)	13(1)
P(3)	4995(1)	2201(1)	5202(1)	13(1)
C(22)	10822(2)	2672(1)	7885(1)	23(1)
C(32)	6515(2)	1691(1)	7830(1)	21(1)
N(1)	6311(1)	3545(1)	6417(1)	13(1)
C(1)	9725(1)	3082(1)	5460(1)	16(1)
C(44)	3364(2)	2993(1)	4302(1)	20(1)
C(21)	9718(2)	3059(1)	7771(1)	20(1)
C(19)	8725(1)	2100(1)	7158(1)	15(1)
C(3)	10384(1)	2762(1)	6053(1)	20(1)
C(39)	7096(2)	1702(1)	3858(1)	25(1)
C(7)	7279(1)	4029(1)	6502(1)	13(1)
C(18)	4542(1)	3123(1)	6884(1)	15(1)
C(45)	2517(2)	3539(1)	4137(1)	22(1)
C(50)	4423(2)	778(1)	5418(1)	21(1)
C(31)	6297(1)	1516(1)	7214(1)	14(1)
C(13)	5201(1)	3687(1)	6657(1)	13(1)
C(48)	3420(1)	3325(1)	5347(1)	16(1)
C(14)	4620(1)	4355(1)	6635(1)	17(1)
C(37)	5473(2)	1836(1)	4505(1)	16(1)
C(43)	3830(1)	2875(1)	4913(1)	15(1)
C(25)	7828(1)	937(1)	6381(1)	16(1)
C(30)	7839(2)	306(1)	6709(1)	23(1)
C(10)	9445(2)	4918(1)	6722(1)	20(1)
C(2)	9830(2)	2595(1)	4918(1)	20(1)
C(6)	6317(2)	4221(1)	4913(1)	22(1)
C(26)	8252(2)	928(1)	5817(1)	20(1)
C(38)	6706(2)	1929(1)	4398(1)	18(1)
C(17)	3366(2)	3223(1)	7061(1)	20(1)
C(15)	3453(2)	4452(1)	6820(1)	20(1)
C(46)	2133(2)	3981(1)	4570(1)	19(1)
C(27)	8694(2)	308(1)	5588(1)	28(1)
C(51)	3728(2)	233(1)	5632(1)	27(1)
C(47)	2583(2)	3870(1)	5177(1)	19(1)
C(8)	8264(1)	3986(1)	6133(1)	14(1)
C(16)	2805(2)	3884(1)	7032(1)	22(1)
C(33)	5640(2)	1511(1)	8212(1)	25(1)

C(12)	7430(1)	4543(1)	6975(1)	16(1)
C(34)	4563(2)	1145(1)	7988(1)	22(1)
C(9)	9316(2)	4430(1)	6254(1)	17(1)
C(20)	8684(2)	2779(1)	7408(1)	16(1)
C(41)	5019(2)	1267(1)	3522(1)	28(1)
C(5)	8478(2)	4286(1)	4596(1)	22(1)
C(53)	2207(2)	1068(1)	5866(1)	31(1)
C(54)	2892(2)	1612(1)	5651(1)	26(1)
C(24)	9837(2)	1712(1)	7279(1)	18(1)
C(29)	8269(2)	-316(1)	6473(1)	31(1)
C(49)	4011(1)	1477(1)	5425(1)	15(1)
C(42)	4635(2)	1487(1)	4061(1)	22(1)
C(35)	4342(2)	968(1)	7379(1)	24(1)
C(11)	8483(2)	4967(1)	7082(1)	19(1)
C(36)	5198(2)	1155(1)	6995(1)	22(1)
C(23)	10882(2)	2001(1)	7635(1)	23(1)
C(4)	7505(2)	3803(1)	4832(1)	17(1)
C(40)	6245(2)	1381(1)	3418(1)	28(1)
C(28)	8695(2)	-315(1)	5916(1)	31(1)
C(52)	2625(2)	378(1)	5858(1)	26(1)

Table 3. Bond lengths [Å] and angles [°] for $PNCu(PPh_3)_2$.

Cu(1)-N(1)	2.0830(12)
Cu(1)-P(1)	2.3173(5)
Cu(1)-P(3)	2.3261(6)
Cu(1)-P(2)	2.3319(5)
P(2)-C(19)	1.8324(16)
P(2)-C(25)	1.8339(15)
P(2)-C(31)	1.8371(15)
P(1)-C(8)	1.8196(15)
P(1)-C(1)	1.8563(15)
P(1)-C(4)	1.8664(16)
P(3)-C(37)	1.8331(15)
P(3)-C(43)	1.8375(15)
P(3)-C(49)	1.8401(15)
C(22)-C(21)	1.388(2)
C(22)-C(23)	1.389(2)
C(22)-H(22)	0.9500
C(32)-C(31)	1.392(2)
C(32)-C(33)	1.394(2)
C(32)-H(32)	0.9500
N(1)-C(7)	1.3796(18)
N(1)-C(13)	1.4012(17)
C(1)-C(3)	1.529(2)
C(1)-C(2)	1.530(2)
C(1)-H(1)	1.0000
C(44)-C(45)	1.391(2)
C(44)-C(43)	1.397(2)
C(44)-H(44)	0.9500
C(21)-C(20)	1.384(2)
C(21)-H(21)	0.9500
C(19)-C(24)	1.396(2)
C(19)-C(20)	1.401(2)

C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(39)-C(40)	1.383(3)
C(39)-C(38)	1.392(2)
C(39)-H(39)	0.9500
C(7)-C(12)	1.420(2)
C(7)-C(8)	1.4303(19)
C(18)-C(17)	1.390(2)
C(18)-C(13)	1.411(2)
C(18)-H(18)	0.9500
C(45)-C(46)	1.382(2)
C(45)-H(45)	0.9500
C(50)-C(49)	1.394(2)
C(50)-C(51)	1.394(2)
C(50)-H(50)	0.9500
C(31)-C(36)	1.393(2)
C(13)-C(14)	1.406(2)
C(48)-C(47)	1.385(2)
C(48)-C(43)	1.401(2)
C(48)-H(48)	0.9500
C(14)-C(15)	1.388(2)
C(14)-H(14)	0.9500
C(37)-C(38)	1.392(2)
C(37)-C(42)	1.404(2)
C(25)-C(26)	1.390(2)
C(25)-C(30)	1.397(2)
C(30)-C(29)	1.392(2)
C(30)-H(30)	0.9500
C(10)-C(9)	1.382(2)
C(10)-C(11)	1.398(2)
C(10)-H(10)	0.9500
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(6)-C(4)	1.535(2)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(26)-C(27)	1.387(2)
C(26)-H(26)	0.9500
C(38)-H(38)	0.9500
C(17)-C(16)	1.385(2)
C(17)-H(17)	0.9500
C(15)-C(16)	1.398(2)
C(15)-H(15)	0.9500
C(46)-C(47)	1.382(2)
C(46)-H(46)	0.9500
C(27)-C(28)	1.385(2)
C(27)-H(27)	0.9500
C(51)-C(52)	1.379(2)
C(51)-H(51)	0.9500
C(47)-H(47)	0.9500
C(8)-C(9)	1.403(2)
C(16)-H(16)	0.9500
C(33)-C(34)	1.381(2)

C(33)-H(33)	0.9500
C(12)-C(11)	1.382(2)
C(12)-H(12)	0.9500
C(34)-C(35)	1.380(2)
C(34)-H(34)	0.9500
C(9)-H(9)	0.9500
C(20)-H(20)	0.9500
C(41)-C(42)	1.383(2)
C(41)-C(40)	1.389(2)
C(41)-H(41)	0.9500
C(5)-C(4)	1.537(2)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(53)-C(52)	1.380(2)
C(53)-C(54)	1.389(2)
C(53)-H(53)	0.9500
C(54)-C(49)	1.392(2)
C(54)-H(54)	0.9500
C(24)-C(23)	1.391(2)
C(24)-H(24)	0.9500
C(29)-C(28)	1.378(2)
C(29)-H(29)	0.9500
C(42)-H(42)	0.9500
C(35)-C(36)	1.385(2)
C(35)-H(35)	0.9500
C(11)-H(11)	0.9500
C(36)-H(36)	0.9500
C(23)-H(23)	0.9500
C(4)-H(4)	1.0000
C(40)-H(40)	0.9500
C(28)-H(28)	0.9500
C(52)-H(52)	0.9500

N(1)-Cu(1)-P(1)	83.53(4)
N(1)-Cu(1)-P(3)	120.36(4)
P(1)-Cu(1)-P(3)	114.664(19)
N(1)-Cu(1)-P(2)	105.35(4)
P(1)-Cu(1)-P(2)	116.61(2)
P(3)-Cu(1)-P(2)	113.145(19)
C(19)-P(2)-C(25)	103.26(7)
C(19)-P(2)-C(31)	102.17(7)
C(25)-P(2)-C(31)	102.57(7)
C(19)-P(2)-Cu(1)	111.75(5)
C(25)-P(2)-Cu(1)	116.62(5)
C(31)-P(2)-Cu(1)	118.44(5)
C(8)-P(1)-C(1)	103.17(7)
C(8)-P(1)-C(4)	104.26(7)
C(1)-P(1)-C(4)	103.68(7)
C(8)-P(1)-Cu(1)	97.74(5)
C(1)-P(1)-Cu(1)	129.23(5)
C(4)-P(1)-Cu(1)	115.16(5)
C(37)-P(3)-C(43)	103.08(7)
C(37)-P(3)-C(49)	100.85(7)
C(43)-P(3)-C(49)	102.66(7)
C(37)-P(3)-Cu(1)	116.79(5)

C(43)-P(3)-Cu(1)	113.56(5)
C(49)-P(3)-Cu(1)	117.74(5)
C(21)-C(22)-C(23)	119.71(15)
C(21)-C(22)-H(22)	120.1
C(23)-C(22)-H(22)	120.1
C(31)-C(32)-C(33)	120.26(15)
C(31)-C(32)-H(32)	119.9
C(33)-C(32)-H(32)	119.9
C(7)-N(1)-C(13)	119.26(11)
C(7)-N(1)-Cu(1)	117.59(9)
C(13)-N(1)-Cu(1)	123.16(9)
C(3)-C(1)-C(2)	111.18(12)
C(3)-C(1)-P(1)	109.67(10)
C(2)-C(1)-P(1)	113.33(11)
C(3)-C(1)-H(1)	107.5
C(2)-C(1)-H(1)	107.5
P(1)-C(1)-H(1)	107.5
C(45)-C(44)-C(43)	120.42(14)
C(45)-C(44)-H(44)	119.8
C(43)-C(44)-H(44)	119.8
C(20)-C(21)-C(22)	120.09(15)
C(20)-C(21)-H(21)	120.0
C(22)-C(21)-H(21)	120.0
C(24)-C(19)-C(20)	118.52(14)
C(24)-C(19)-P(2)	123.83(11)
C(20)-C(19)-P(2)	117.60(12)
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(40)-C(39)-C(38)	119.63(16)
C(40)-C(39)-H(39)	120.2
C(38)-C(39)-H(39)	120.2
N(1)-C(7)-C(12)	124.03(13)
N(1)-C(7)-C(8)	119.33(12)
C(12)-C(7)-C(8)	116.41(13)
C(17)-C(18)-C(13)	121.50(14)
C(17)-C(18)-H(18)	119.3
C(13)-C(18)-H(18)	119.3
C(46)-C(45)-C(44)	120.95(15)
C(46)-C(45)-H(45)	119.5
C(44)-C(45)-H(45)	119.5
C(49)-C(50)-C(51)	120.58(15)
C(49)-C(50)-H(50)	119.7
C(51)-C(50)-H(50)	119.7
C(32)-C(31)-C(36)	118.40(14)
C(32)-C(31)-P(2)	123.69(12)
C(36)-C(31)-P(2)	117.78(11)
N(1)-C(13)-C(14)	123.86(13)
N(1)-C(13)-C(18)	119.32(13)
C(14)-C(13)-C(18)	116.51(13)
C(47)-C(48)-C(43)	121.32(15)
C(47)-C(48)-H(48)	119.3
C(43)-C(48)-H(48)	119.3

C(15)-C(14)-C(13)	121.65(14)
C(15)-C(14)-H(14)	119.2
C(13)-C(14)-H(14)	119.2
C(38)-C(37)-C(42)	118.23(14)
C(38)-C(37)-P(3)	119.00(12)
C(42)-C(37)-P(3)	122.73(12)
C(44)-C(43)-C(48)	117.81(14)
C(44)-C(43)-P(3)	125.62(11)
C(48)-C(43)-P(3)	116.52(12)
C(26)-C(25)-C(30)	118.61(14)
C(26)-C(25)-P(2)	117.92(11)
C(30)-C(25)-P(2)	123.45(12)
C(29)-C(30)-C(25)	120.18(15)
C(29)-C(30)-H(30)	119.9
C(25)-C(30)-H(30)	119.9
C(9)-C(10)-C(11)	118.09(15)
C(9)-C(10)-H(10)	121.0
C(11)-C(10)-H(10)	121.0
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(27)-C(26)-C(25)	121.00(15)
C(27)-C(26)-H(26)	119.5
C(25)-C(26)-H(26)	119.5
C(39)-C(38)-C(37)	121.23(16)
C(39)-C(38)-H(38)	119.4
C(37)-C(38)-H(38)	119.4
C(16)-C(17)-C(18)	121.16(14)
C(16)-C(17)-H(17)	119.4
C(18)-C(17)-H(17)	119.4
C(14)-C(15)-C(16)	120.94(14)
C(14)-C(15)-H(15)	119.5
C(16)-C(15)-H(15)	119.5
C(45)-C(46)-C(47)	119.25(15)
C(45)-C(46)-H(46)	120.4
C(47)-C(46)-H(46)	120.4
C(28)-C(27)-C(26)	119.85(16)
C(28)-C(27)-H(27)	120.1
C(26)-C(27)-H(27)	120.1
C(52)-C(51)-C(50)	120.57(15)
C(52)-C(51)-H(51)	119.7
C(50)-C(51)-H(51)	119.7
C(46)-C(47)-C(48)	120.25(14)
C(46)-C(47)-H(47)	119.9
C(48)-C(47)-H(47)	119.9
C(9)-C(8)-C(7)	120.01(13)
C(9)-C(8)-P(1)	123.97(11)

C(7)-C(8)-P(1)	115.96(11)
C(17)-C(16)-C(15)	118.22(14)
C(17)-C(16)-H(16)	120.9
C(15)-C(16)-H(16)	120.9
C(34)-C(33)-C(32)	120.52(16)
C(34)-C(33)-H(33)	119.7
C(32)-C(33)-H(33)	119.7
C(11)-C(12)-C(7)	121.98(14)
C(11)-C(12)-H(12)	119.0
C(7)-C(12)-H(12)	119.0
C(35)-C(34)-C(33)	119.56(15)
C(35)-C(34)-H(34)	120.2
C(33)-C(34)-H(34)	120.2
C(10)-C(9)-C(8)	122.30(14)
C(10)-C(9)-H(9)	118.9
C(8)-C(9)-H(9)	118.9
C(21)-C(20)-C(19)	120.92(15)
C(21)-C(20)-H(20)	119.5
C(19)-C(20)-H(20)	119.5
C(42)-C(41)-C(40)	120.33(17)
C(42)-C(41)-H(41)	119.8
C(40)-C(41)-H(41)	119.8
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(52)-C(53)-C(54)	120.28(16)
C(52)-C(53)-H(53)	119.9
C(54)-C(53)-H(53)	119.9
C(53)-C(54)-C(49)	121.15(15)
C(53)-C(54)-H(54)	119.4
C(49)-C(54)-H(54)	119.4
C(23)-C(24)-C(19)	120.45(14)
C(23)-C(24)-H(24)	119.8
C(19)-C(24)-H(24)	119.8
C(28)-C(29)-C(30)	120.40(16)
C(28)-C(29)-H(29)	119.8
C(30)-C(29)-H(29)	119.8
C(54)-C(49)-C(50)	118.03(14)
C(54)-C(49)-P(3)	121.39(11)
C(50)-C(49)-P(3)	120.39(12)
C(41)-C(42)-C(37)	120.50(16)
C(41)-C(42)-H(42)	119.8
C(37)-C(42)-H(42)	119.8
C(34)-C(35)-C(36)	120.17(16)
C(34)-C(35)-H(35)	119.9
C(36)-C(35)-H(35)	119.9
C(12)-C(11)-C(10)	121.20(14)
C(12)-C(11)-H(11)	119.4
C(10)-C(11)-H(11)	119.4
C(35)-C(36)-C(31)	121.08(15)
C(35)-C(36)-H(36)	119.5
C(31)-C(36)-H(36)	119.5
C(22)-C(23)-C(24)	120.30(15)

C(22)-C(23)-H(23)	119.8
C(24)-C(23)-H(23)	119.8
C(6)-C(4)-C(5)	110.70(12)
C(6)-C(4)-P(1)	109.93(10)
C(5)-C(4)-P(1)	115.18(12)
C(6)-C(4)-H(4)	106.9
C(5)-C(4)-H(4)	106.9
P(1)-C(4)-H(4)	106.9
C(39)-C(40)-C(41)	120.02(15)
C(39)-C(40)-H(40)	120.0
C(41)-C(40)-H(40)	120.0
C(29)-C(28)-C(27)	119.95(15)
C(29)-C(28)-H(28)	120.0
C(27)-C(28)-H(28)	120.0
C(51)-C(52)-C(53)	119.39(15)
C(51)-C(52)-H(52)	120.3
C(53)-C(52)-H(52)	120.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $PNCu(PPh_3)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	12(1)	12(1)	13(1)	0(1)	3(1)	1(1)
P(2)	14(1)	12(1)	12(1)	1(1)	2(1)	0(1)
P(1)	12(1)	13(1)	14(1)	1(1)	3(1)	1(1)
P(3)	13(1)	14(1)	13(1)	-1(1)	1(1)	2(1)
C(22)	18(1)	28(1)	21(1)	1(1)	-3(1)	-7(1)
C(32)	20(1)	25(1)	17(1)	-1(1)	3(1)	-5(1)
N(1)	11(1)	12(1)	17(1)	-1(1)	3(1)	0(1)
C(1)	12(1)	17(1)	19(1)	1(1)	5(1)	1(1)
C(44)	22(1)	22(1)	16(1)	1(1)	4(1)	4(1)
C(21)	22(1)	19(1)	19(1)	-1(1)	3(1)	-4(1)
C(19)	16(1)	16(1)	13(1)	3(1)	2(1)	-3(1)
C(3)	14(1)	25(1)	21(1)	1(1)	4(1)	5(1)
C(39)	32(1)	23(1)	23(1)	-1(1)	13(1)	4(1)
C(7)	14(1)	11(1)	13(1)	3(1)	1(1)	4(1)
C(18)	14(1)	18(1)	14(1)	-2(1)	3(1)	1(1)
C(45)	22(1)	27(1)	17(1)	6(1)	0(1)	5(1)
C(50)	28(1)	18(1)	18(1)	-2(1)	6(1)	4(1)
C(31)	15(1)	13(1)	15(1)	3(1)	3(1)	1(1)
C(13)	11(1)	17(1)	11(1)	-4(1)	0(1)	0(1)
C(48)	16(1)	17(1)	14(1)	0(1)	-1(1)	1(1)
C(14)	17(1)	16(1)	17(1)	-3(1)	2(1)	1(1)
C(37)	19(1)	14(1)	14(1)	-1(1)	2(1)	4(1)
C(43)	12(1)	15(1)	17(1)	0(1)	2(1)	-2(1)
C(25)	14(1)	15(1)	17(1)	0(1)	0(1)	0(1)
C(30)	29(1)	19(1)	24(1)	2(1)	6(1)	3(1)
C(10)	16(1)	18(1)	23(1)	1(1)	0(1)	-3(1)
C(2)	18(1)	21(1)	21(1)	0(1)	6(1)	3(1)
C(6)	18(1)	20(1)	26(1)	6(1)	0(1)	2(1)
C(26)	20(1)	20(1)	20(1)	0(1)	4(1)	1(1)
C(38)	22(1)	15(1)	17(1)	0(1)	4(1)	3(1)

C(17)	15(1)	29(1)	17(1)	0(1)	4(1)	-4(1)
C(15)	17(1)	24(1)	20(1)	-6(1)	0(1)	7(1)
C(46)	15(1)	16(1)	24(1)	5(1)	2(1)	2(1)
C(27)	27(1)	32(1)	25(1)	-9(1)	7(1)	2(1)
C(51)	45(1)	13(1)	23(1)	-2(1)	7(1)	2(1)
C(47)	19(1)	15(1)	22(1)	-2(1)	4(1)	0(1)
C(8)	14(1)	13(1)	15(1)	1(1)	2(1)	2(1)
C(16)	14(1)	34(1)	18(1)	-6(1)	4(1)	3(1)
C(33)	28(1)	32(1)	14(1)	-1(1)	6(1)	-5(1)
C(12)	16(1)	14(1)	17(1)	0(1)	2(1)	2(1)
C(34)	23(1)	23(1)	22(1)	4(1)	10(1)	-1(1)
C(9)	16(1)	16(1)	20(1)	4(1)	4(1)	-1(1)
C(20)	18(1)	17(1)	14(1)	2(1)	3(1)	1(1)
C(41)	38(1)	26(1)	17(1)	-5(1)	-6(1)	6(1)
C(5)	25(1)	22(1)	22(1)	8(1)	8(1)	3(1)
C(53)	18(1)	28(1)	49(1)	10(1)	11(1)	1(1)
C(54)	20(1)	16(1)	45(1)	6(1)	11(1)	5(1)
C(24)	21(1)	17(1)	17(1)	2(1)	1(1)	1(1)
C(29)	38(1)	15(1)	41(1)	1(1)	7(1)	4(1)
C(49)	15(1)	15(1)	14(1)	-2(1)	-2(1)	0(1)
C(42)	24(1)	21(1)	19(1)	-2(1)	-1(1)	5(1)
C(35)	20(1)	29(1)	22(1)	4(1)	3(1)	-9(1)
C(11)	21(1)	16(1)	19(1)	-3(1)	-1(1)	-1(1)
C(36)	25(1)	29(1)	13(1)	2(1)	2(1)	-9(1)
C(23)	16(1)	28(1)	23(1)	6(1)	0(1)	4(1)
C(4)	20(1)	15(1)	16(1)	2(1)	1(1)	0(1)
C(40)	45(1)	25(1)	16(1)	-2(1)	9(1)	9(1)
C(28)	32(1)	20(1)	42(1)	-11(1)	7(1)	4(1)
C(52)	32(1)	19(1)	27(1)	3(1)	0(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $PNCu(PPh_3)_2$.

	x	y	z	U(eq)
H(22)	11533	2865	8132	27
H(32)	7262	1933	7990	25
H(1)	10167	3534	5389	19
H(44)	3628	2699	3997	24
H(21)	9673	3518	7941	24
H(3A)	10070	2281	6100	30
H(3B)	10215	3054	6397	30
H(3C)	11291	2746	6042	30
H(39)	7942	1768	3793	30
H(18)	4910	2665	6916	19
H(45)	2198	3608	3720	27
H(50)	5183	672	5266	25
H(48)	3721	3254	5766	19
H(14)	5036	4750	6489	20
H(30)	7553	301	7095	28
H(10)	10167	5211	6797	23
H(2A)	10713	2549	4862	30
H(2B)	9351	2796	4550	30

H(2C)	9493	2127	4997	30
H(6A)	6537	4609	5201	32
H(6B)	5714	3906	5069	32
H(6C)	5942	4416	4519	32
H(26)	8238	1351	5586	24
H(38)	7293	2152	4699	21
H(17)	2940	2830	7204	25
H(15)	3089	4911	6802	24
H(46)	1565	4358	4452	22
H(27)	8996	312	5206	33
H(51)	4016	-241	5622	32
H(47)	2318	4168	5479	22
H(16)	2001	3949	7153	26
H(33)	5787	1641	8629	29
H(12)	6788	4595	7224	19
H(34)	3977	1017	8251	26
H(9)	9962	4393	6005	21
H(20)	7936	3050	7328	19
H(41)	4440	1038	3221	33
H(5A)	8089	4531	4228	34
H(5B)	9184	4000	4500	34
H(5C)	8782	4635	4908	34
H(53)	1446	1171	6019	37
H(54)	2592	2084	5657	32
H(24)	9880	1249	7117	22
H(29)	8268	-745	6697	37
H(42)	3797	1400	4130	26
H(35)	3601	718	7222	28
H(11)	8555	5299	7407	23
H(36)	5033	1034	6576	27
H(23)	11640	1737	7708	27
H(4)	7252	3441	4509	20
H(40)	6499	1238	3043	34
H(28)	8989	-740	5758	37
H(52)	2158	6	6006	32

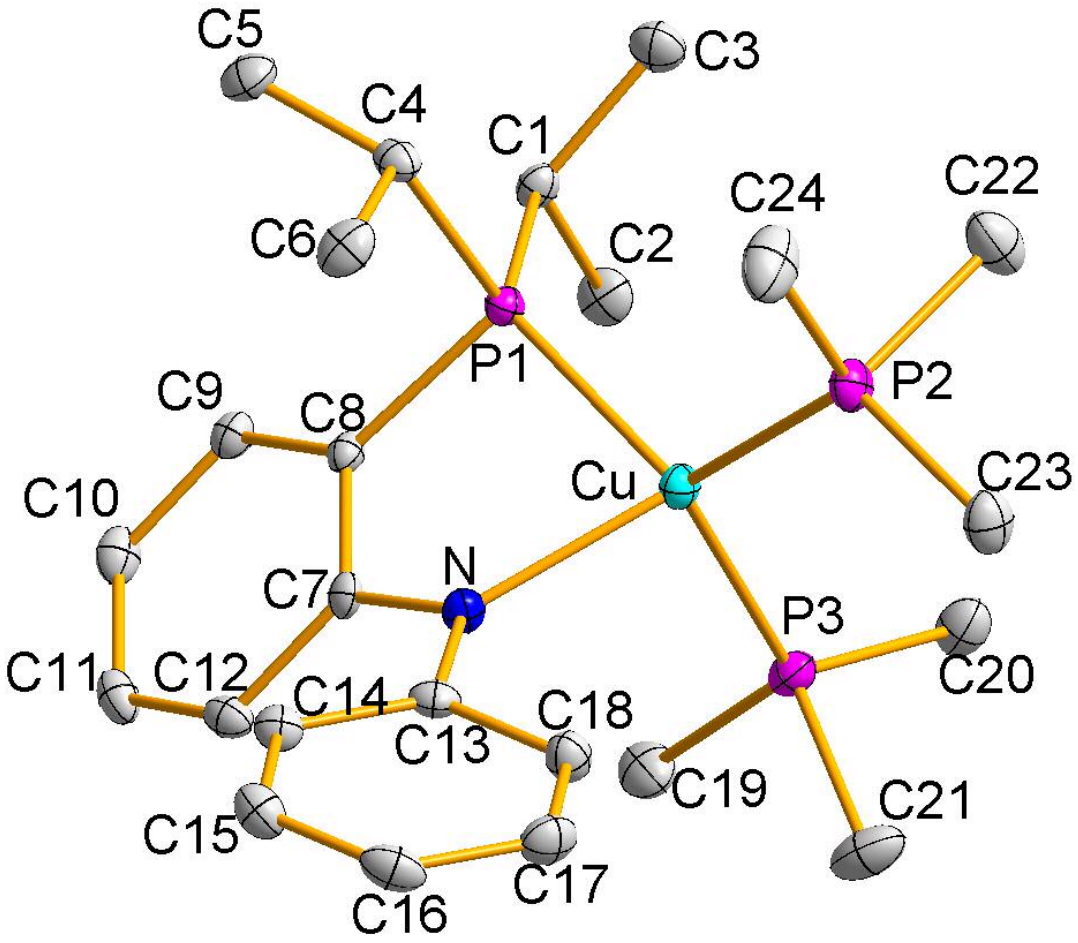

Figure S25. Fully numbered molecular structure of **3**. Hydrogen atoms omitted for clarity.

$PNCu(PMe_3)_2$ (**3**)

Table 1. Crystal data and structure refinement for $PNCu(PMe_3)_2$.

Identification code	$PNCu(PMe_3)_2$	
Empirical formula	C24 H41 Cu N P3	
Formula weight	500.03	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.9195(4) Å	α= 90°.
	b = 16.3588(7) Å	β= 90°.
	c = 16.5646(7) Å	γ = 90°.
Volume	2687.96(19) $Å^3$	
Z	4	
Density (calculated)	1.236 Mg/m^3	
Absorption coefficient	1.002 mm^{-1}	
F(000)	1064	
Crystal size	0.444 x 0.148 x 0.130 mm^3	

Theta range for data collection	1.75 to 38.21°.
Index ranges	-14≤h≤17, -27≤k≤27, -20≤l≤28
Reflections collected	36846
Independent reflections	12091 [R(int) = 0.0750]
Completeness to theta = 38.21°	91.1 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12091 / 0 / 272
Goodness-of-fit on F^2	1.070
Final R indices [I>2σ(I)]	R1 = 0.0424, wR2 = 0.0615
R indices (all data)	R1 = 0.0734, wR2 = 0.0660
Absolute structure parameter	-0.025(7)
Largest diff. peak and hole	1.574 and -0.627 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $PNCu(PMe_3)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5897(2)	5983(1)	8325(1)	14(1)
C(2)	5086(2)	6749(1)	8545(1)	20(1)
C(3)	5428(2)	5648(1)	7508(1)	21(1)
C(4)	6906(2)	4379(1)	8818(1)	15(1)
C(5)	8337(2)	4694(1)	8662(1)	20(1)
C(6)	6941(2)	3707(1)	9465(1)	20(1)
C(7)	5923(2)	5272(1)	10757(1)	12(1)
C(8)	6423(2)	5611(1)	10024(1)	12(1)
C(9)	7399(2)	6232(1)	10038(1)	14(1)
C(10)	7886(2)	6537(1)	10761(1)	17(1)
C(11)	7386(2)	6225(1)	11482(1)	17(1)
C(12)	6431(2)	5611(1)	11484(1)	15(1)
C(13)	4795(2)	4091(1)	11304(1)	14(1)
C(14)	5854(2)	3817(1)	11808(1)	15(1)
C(15)	5663(2)	3192(1)	12360(1)	18(1)
C(16)	4432(2)	2803(1)	12441(1)	21(1)
C(17)	3375(2)	3058(1)	11948(1)	20(1)
C(18)	3554(2)	3682(1)	11391(1)	18(1)
C(19)	3176(2)	6591(1)	10694(1)	24(1)
C(20)	1240(2)	6370(1)	9444(1)	23(1)
C(21)	1124(2)	5426(1)	10879(1)	29(1)
C(22)	2075(2)	4013(1)	8083(1)	29(1)
C(23)	1129(2)	3307(1)	9541(1)	22(1)
C(24)	3594(2)	2793(1)	8885(1)	32(1)
Cu	3714(1)	4775(1)	9688(1)	13(1)
N	4924(1)	4683(1)	10714(1)	13(1)
P(1)	5679(1)	5191(1)	9112(1)	11(1)
P(2)	2660(1)	3730(1)	9093(1)	17(1)
P(3)	2325(1)	5785(1)	10123(1)	16(1)

Table 3. Bond lengths [Å] and angles [°] for $PNCu(PMe_3)_2$.

C(1)-C(2)	1.532(2)
C(1)-C(3)	1.533(3)
C(1)-P(1)	1.8506(17)

C(1)-H(1)	1.0000
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-C(5)	1.531(2)
C(4)-C(6)	1.535(2)
C(4)-P(1)	1.8654(18)
C(4)-H(4)	1.0000
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-N	1.385(2)
C(7)-C(12)	1.418(2)
C(7)-C(8)	1.424(2)
C(8)-C(9)	1.403(2)
C(8)-P(1)	1.8165(17)
C(9)-C(10)	1.384(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.390(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.381(2)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-N	1.382(2)
C(13)-C(18)	1.409(3)
C(13)-C(14)	1.414(2)
C(14)-C(15)	1.386(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.383(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.394(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.387(2)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-P(3)	1.829(2)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-P(3)	1.8261(19)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-P(3)	1.8267(19)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-P(2)	1.830(2)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800

C(22)-H(22C)	0.9800
C(23)-P(2)	1.8259(19)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-P(2)	1.824(2)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
Cu-N	2.0862(14)
Cu-P(2)	2.2331(5)
Cu-P(3)	2.2690(5)
Cu-P(1)	2.2744(5)

C(2)-C(1)-C(3)	110.06(15)
C(2)-C(1)-P(1)	110.13(12)
C(3)-C(1)-P(1)	109.67(12)
C(2)-C(1)-H(1)	109.0
C(3)-C(1)-H(1)	109.0
P(1)-C(1)-H(1)	109.0
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(5)-C(4)-C(6)	109.75(15)
C(5)-C(4)-P(1)	114.17(12)
C(6)-C(4)-P(1)	110.01(12)
C(5)-C(4)-H(4)	107.5
C(6)-C(4)-H(4)	107.5
P(1)-C(4)-H(4)	107.5
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
N-C(7)-C(12)	124.71(16)
N-C(7)-C(8)	118.48(15)
C(12)-C(7)-C(8)	116.67(15)
C(9)-C(8)-C(7)	120.50(15)
C(9)-C(8)-P(1)	124.65(13)
C(7)-C(8)-P(1)	114.84(12)

C(10)-C(9)-C(8)	121.09(17)
C(10)-C(9)-H(9)	119.5
C(8)-C(9)-H(9)	119.5
C(9)-C(10)-C(11)	119.09(16)
C(9)-C(10)-H(10)	120.5
C(11)-C(10)-H(10)	120.5
C(12)-C(11)-C(10)	120.95(17)
C(12)-C(11)-H(11)	119.5
C(10)-C(11)-H(11)	119.5
C(11)-C(12)-C(7)	121.68(17)
C(11)-C(12)-H(12)	119.2
C(7)-C(12)-H(12)	119.2
N-C(13)-C(18)	119.08(16)
N-C(13)-C(14)	124.76(16)
C(18)-C(13)-C(14)	116.03(16)
C(15)-C(14)-C(13)	121.45(18)
C(15)-C(14)-H(14)	119.3
C(13)-C(14)-H(14)	119.3
C(16)-C(15)-C(14)	121.64(18)
C(16)-C(15)-H(15)	119.2
C(14)-C(15)-H(15)	119.2
C(15)-C(16)-C(17)	117.95(17)
C(15)-C(16)-H(16)	121.0
C(17)-C(16)-H(16)	121.0
C(18)-C(17)-C(16)	120.99(18)
C(18)-C(17)-H(17)	119.5
C(16)-C(17)-H(17)	119.5
C(17)-C(18)-C(13)	121.93(18)
C(17)-C(18)-H(18)	119.0
C(13)-C(18)-H(18)	119.0
P(3)-C(19)-H(19A)	109.5
P(3)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
P(3)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
P(3)-C(20)-H(20A)	109.5
P(3)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
P(3)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
P(3)-C(21)-H(21A)	109.5
P(3)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
P(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
P(2)-C(22)-H(22A)	109.5
P(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
P(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
P(2)-C(23)-H(23A)	109.5
P(2)-C(23)-H(23B)	109.5

H(23A)-C(23)-H(23B)	109.5
P(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
P(2)-C(24)-H(24A)	109.5
P(2)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
P(2)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
N-Cu-P(2)	124.98(4)
N-Cu-P(3)	98.28(4)
P(2)-Cu-P(3)	114.41(2)
N-Cu-P(1)	82.54(4)
P(2)-Cu-P(1)	116.406(19)
P(3)-Cu-P(1)	115.86(2)
C(13)-N-C(7)	121.22(15)
C(13)-N-Cu	125.00(12)
C(7)-N-Cu	113.76(11)
C(8)-P(1)-C(1)	105.84(8)
C(8)-P(1)-C(4)	102.78(8)
C(1)-P(1)-C(4)	103.82(8)
C(8)-P(1)-Cu	96.46(6)
C(1)-P(1)-Cu	127.20(6)
C(4)-P(1)-Cu	117.12(6)
C(24)-P(2)-C(23)	100.43(10)
C(24)-P(2)-C(22)	101.57(10)
C(23)-P(2)-C(22)	101.70(10)
C(24)-P(2)-Cu	119.29(7)
C(23)-P(2)-Cu	120.00(6)
C(22)-P(2)-Cu	111.00(7)
C(20)-P(3)-C(21)	101.94(10)
C(20)-P(3)-C(19)	102.33(9)
C(21)-P(3)-C(19)	100.29(10)
C(20)-P(3)-Cu	122.93(7)
C(21)-P(3)-Cu	112.28(6)
C(19)-P(3)-Cu	114.09(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $PNCu(PMe_3)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	12(1)	14(1)	15(1)	2(1)	2(1)	-1(1)
C(2)	23(1)	16(1)	21(1)	5(1)	-1(1)	3(1)
C(3)	23(1)	23(1)	16(1)	3(1)	0(1)	-1(1)
C(4)	18(1)	15(1)	13(1)	-2(1)	-1(1)	3(1)
C(5)	18(1)	20(1)	22(1)	0(1)	4(1)	5(1)
C(6)	21(1)	13(1)	28(1)	2(1)	3(1)	4(1)
C(7)	9(1)	11(1)	15(1)	1(1)	-2(1)	1(1)
C(8)	10(1)	11(1)	14(1)	-2(1)	0(1)	0(1)
C(9)	12(1)	13(1)	18(1)	0(1)	1(1)	0(1)
C(10)	15(1)	12(1)	25(1)	-3(1)	-3(1)	-2(1)
C(11)	19(1)	14(1)	19(1)	-4(1)	-7(1)	3(1)

C(12)	19(1)	14(1)	12(1)	0(1)	-1(1)	3(1)
C(13)	19(1)	12(1)	12(1)	-2(1)	2(1)	1(1)
C(14)	17(1)	12(1)	16(1)	-1(1)	0(1)	0(1)
C(15)	23(1)	14(1)	18(1)	0(1)	-5(1)	1(1)
C(16)	33(1)	16(1)	14(1)	2(1)	2(1)	-2(1)
C(17)	19(1)	20(1)	21(1)	0(1)	5(1)	-5(1)
C(18)	16(1)	19(1)	17(1)	1(1)	-1(1)	-3(1)
C(19)	25(1)	21(1)	26(1)	-3(1)	-2(1)	8(1)
C(20)	19(1)	24(1)	26(1)	7(1)	2(1)	1(1)
C(21)	30(1)	27(1)	29(1)	8(1)	14(1)	7(1)
C(22)	32(1)	34(1)	22(1)	3(1)	-6(1)	-10(1)
C(23)	19(1)	21(1)	27(1)	3(1)	-3(1)	-6(1)
C(24)	24(1)	24(1)	50(1)	-13(1)	-4(1)	-3(1)
Cu	12(1)	13(1)	14(1)	1(1)	0(1)	-2(1)
N	13(1)	13(1)	14(1)	2(1)	0(1)	-2(1)
P(1)	12(1)	11(1)	11(1)	0(1)	0(1)	-1(1)
P(2)	15(1)	15(1)	19(1)	-1(1)	-1(1)	-3(1)
P(3)	14(1)	17(1)	17(1)	3(1)	3(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $PNCu(PMe_3)_2$.

	x	y	z	U(eq)
H(1)	6873	6130	8288	16
H(2A)	4124	6614	8559	30
H(2B)	5246	7174	8139	30
H(2C)	5371	6947	9076	30
H(3A)	5570	6063	7089	31
H(3B)	4468	5510	7537	31
H(3C)	5947	5157	7374	31
H(4)	6574	4125	8307	18
H(5A)	8906	4241	8477	30
H(5B)	8709	4921	9162	30
H(5C)	8310	5120	8246	30
H(6A)	7293	3934	9971	31
H(6B)	7525	3261	9284	31
H(6C)	6027	3499	9554	31
H(9)	7731	6446	9544	17
H(10)	8552	6954	10764	21
H(11)	7706	6438	11980	20
H(12)	6106	5410	11985	18
H(14)	6715	4067	11766	18
H(15)	6395	3026	12692	22
H(16)	4311	2374	12822	25
H(17)	2519	2802	11993	24
H(18)	2817	3838	11058	21
H(19A)	2504	6964	10921	36
H(19B)	3780	6895	10334	36
H(19C)	3702	6345	11132	36
H(20A)	711	6763	9757	34
H(20B)	630	5996	9160	34
H(20C)	1797	6663	9050	34
H(21A)	490	5042	10628	43

H(21B)	626	5892	11100	43
H(21C)	1611	5149	11315	43
H(22A)	1536	3566	7858	44
H(22B)	2853	4116	7734	44
H(22C)	1521	4508	8118	44
H(23A)	1334	3091	10079	33
H(23B)	785	2866	9198	33
H(23C)	447	3738	9586	33
H(24A)	4356	2916	8528	49
H(24B)	2998	2397	8621	49
H(24C)	3930	2563	9392	49

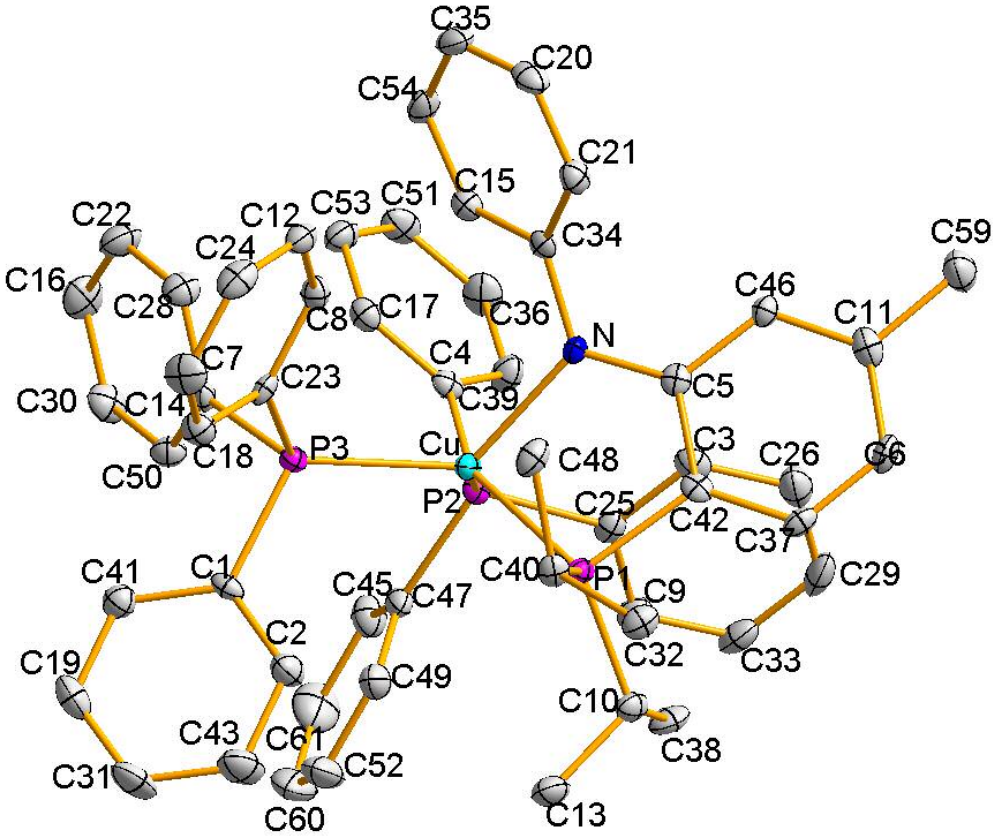

Figure S26. Fully numbered molecular structure of **7**. Hydrogen atoms omitted for clarity.

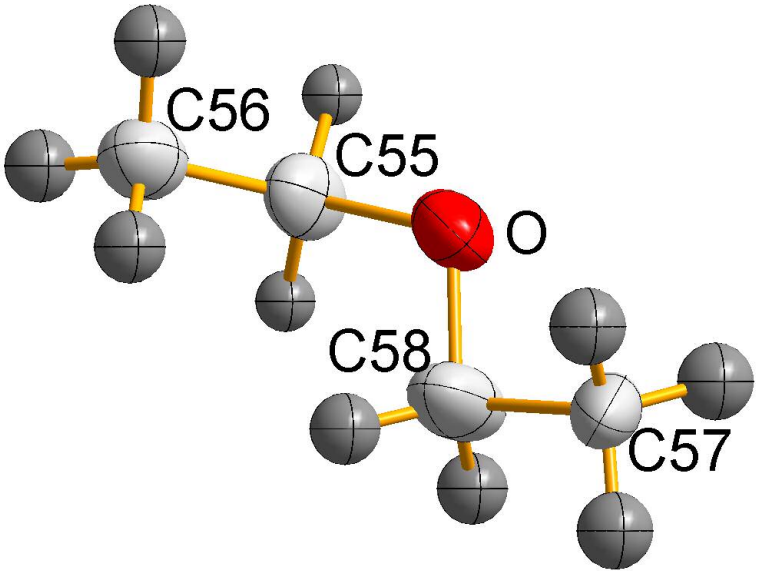

Figure S27. Diethyl ether molecule crystallized with **7**.

^{Me}PNCu(PPh$_3$)$_2$ (**7**)

Table 1. Crystal data and structure refinement for ^{Me}PNCu(PPh$_3$)$_2$.

Identification code	^{Me}PNCu(PPh$_3$)$_2$	
Empirical formula	C59 H65 Cu N O P3	
Formula weight	960.57	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.099(4) Å	α= 90°.
	b = 21.513(7) Å	β= 103.72(3)°.
	c = 21.933(6) Å	γ = 90°.
Volume	5088(3) Å^3	
Z	4	
Density (calculated)	1.254 Mg/m^3	
Absorption coefficient	0.565 mm^{-1}	
F(000)	2032	
Crystal size	0.407 x 0.1184 x 0.111 mm^3	
Theta range for data collection	1.89 to 28.31°.	
Index ranges	-14≤h≤13, -27≤k≤28, -25≤l≤28	
Reflections collected	32529	
Independent reflections	11108 [R(int) = 0.0711]	
Completeness to theta = 28.31°	87.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11108 / 0 / 593	
Goodness-of-fit on F^2	1.589	
Final R indices [I>2σ(I)]	R1 = 0.0497, wR2 = 0.0938	
R indices (all data)	R1 = 0.0732, wR2 = 0.0974	
Largest diff. peak and hole	0.770 and -0.589 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $^{Me}PNCu(PPh_3)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu	2313(1)	4290(1)	2852(1)	13(1)
P(1)	1103(1)	4639(1)	3515(1)	12(1)
P(2)	1318(1)	3637(1)	2031(1)	13(1)
P(3)	3479(1)	5035(1)	2486(1)	12(1)
C(1)	2644(2)	5733(1)	2130(1)	14(1)
C(2)	1663(3)	5944(1)	2361(1)	22(1)
C(3)	475(3)	2850(1)	2836(1)	20(1)
C(4)	2117(2)	3027(1)	1681(1)	14(1)
C(5)	2378(2)	3600(1)	4039(1)	13(1)
C(6)	695(2)	3268(1)	4775(1)	19(1)
C(7)	6032(3)	6242(1)	3567(1)	25(1)
C(8)	5571(2)	4981(1)	3484(1)	16(1)
C(9)	-1114(2)	3127(1)	1924(1)	20(1)
N	3084(2)	3737(1)	3621(1)	12(1)
C(10)	-579(2)	4823(1)	3366(1)	17(1)
C(11)	1761(3)	2915(1)	4811(1)	18(1)
C(12)	6550(2)	5213(1)	3941(1)	19(1)
C(13)	-889(3)	5455(1)	3054(1)	24(1)
C(14)	4164(2)	4752(1)	1854(1)	13(1)
C(15)	4821(2)	3395(1)	3220(1)	16(1)
C(16)	5148(3)	4236(1)	901(1)	29(1)
C(17)	3294(2)	3137(1)	1589(1)	17(1)
C(18)	5058(2)	6015(1)	3101(1)	20(1)
C(19)	2377(3)	6620(1)	1437(1)	25(1)
C(20)	6402(2)	3413(1)	4394(1)	22(1)
C(21)	5155(2)	3542(1)	4330(1)	17(1)
C(22)	5854(3)	4261(1)	1510(1)	27(1)
C(23)	4809(2)	5379(1)	3058(1)	13(1)
C(24)	6773(2)	5842(1)	3989(1)	22(1)
C(25)	121(2)	3171(1)	2267(1)	16(1)
C(26)	-370(3)	2499(1)	3053(2)	27(1)
C(28)	5370(2)	4518(1)	1985(1)	21(1)
C(29)	-1599(3)	2461(1)	2711(2)	29(1)
C(30)	3950(3)	4463(1)	769(1)	24(1)
C(31)	1391(3)	6825(1)	1666(2)	31(1)
C(32)	1134(2)	5415(1)	4576(1)	19(1)
C(33)	-1951(3)	2775(1)	2148(1)	24(1)
C(34)	4327(2)	3544(1)	3735(1)	13(1)
C(35)	6874(3)	3276(1)	3880(2)	25(1)
C(36)	2184(3)	2001(1)	1234(1)	25(1)
C(37)	486(2)	3789(1)	4389(1)	16(1)
C(38)	-1343(2)	4309(1)	2971(1)	22(1)
C(39)	1563(3)	2447(1)	1503(1)	20(1)
C(40)	1821(2)	5277(1)	4063(1)	16(1)
C(41)	2996(2)	6081(1)	1662(1)	19(1)
C(42)	1297(2)	3962(1)	4028(1)	13(1)
C(43)	1037(3)	6491(1)	2136(2)	31(1)
O	3095(2)	3882(1)	9373(1)	51(1)
C(45)	10(3)	3798(1)	754(1)	25(1)
C(46)	2585(2)	3082(1)	4453(1)	14(1)
C(47)	406(2)	4056(1)	1345(1)	17(1)

C(48)	3187(2)	5132(1)	4351(1)	19(1)
C(49)	28(3)	4657(1)	1444(1)	24(1)
C(50)	3461(2)	4712(1)	1242(1)	18(1)
C(51)	3348(3)	2119(1)	1145(1)	24(1)
C(52)	-717(3)	4997(2)	969(2)	37(1)
C(53)	3904(3)	2689(1)	1318(1)	21(1)
C(54)	6064(2)	3269(1)	3291(1)	21(1)
C(59)	2015(3)	2346(1)	5235(2)	28(1)
C(55)	3907(3)	3999(2)	8960(2)	44(1)
C(57)	1749(4)	3247(2)	9743(2)	56(1)
C(58)	2620(4)	3278(2)	9330(2)	60(1)
C(56)	3193(3)	4130(2)	8313(2)	50(1)
C(60)	-1103(3)	4732(2)	384(2)	43(1)
C(61)	-740(3)	4141(2)	271(2)	40(1)

Table 3. Bond lengths [Å] and angles [°] for $^{Me}PNCu(PPh_3)_2$.

Cu-N	2.076(2)
Cu-P(3)	2.3189(9)
Cu-P(1)	2.3261(10)
Cu-P(2)	2.3439(9)
P(1)-C(42)	1.822(3)
P(1)-C(10)	1.860(3)
P(1)-C(40)	1.873(3)
P(2)-C(25)	1.833(3)
P(2)-C(47)	1.838(3)
P(2)-C(4)	1.850(3)
P(3)-C(14)	1.836(3)
P(3)-C(1)	1.838(3)
P(3)-C(23)	1.850(3)
C(1)-C(2)	1.382(4)
C(1)-C(41)	1.398(4)
C(2)-C(43)	1.396(4)
C(2)-H(2)	0.9500
C(3)-C(26)	1.374(4)
C(3)-C(25)	1.399(4)
C(3)-H(3)	0.9500
C(4)-C(17)	1.388(4)
C(4)-C(39)	1.405(4)
C(5)-N	1.371(3)
C(5)-C(46)	1.423(4)
C(5)-C(42)	1.425(3)
C(6)-C(37)	1.391(4)
C(6)-C(11)	1.393(4)
C(6)-H(6)	0.9500
C(7)-C(24)	1.383(4)
C(7)-C(18)	1.388(4)
C(7)-H(7)	0.9500
C(8)-C(12)	1.385(3)
C(8)-C(23)	1.396(3)
C(8)-H(8)	0.9500
C(9)-C(33)	1.377(4)
C(9)-C(25)	1.401(4)
C(9)-H(9)	0.9500

N-C(34)	1.405(3)
C(10)-C(13)	1.525(4)
C(10)-C(38)	1.530(4)
C(10)-H(10)	1.0000
C(11)-C(46)	1.385(4)
C(11)-C(59)	1.523(4)
C(12)-C(24)	1.376(4)
C(12)-H(12)	0.9500
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(50)	1.387(4)
C(14)-C(28)	1.395(4)
C(15)-C(54)	1.379(4)
C(15)-C(34)	1.405(4)
C(15)-H(15)	0.9500
C(16)-C(22)	1.379(4)
C(16)-C(30)	1.381(4)
C(16)-H(16)	0.9500
C(17)-C(53)	1.390(4)
C(17)-H(17)	0.9500
C(18)-C(23)	1.394(3)
C(18)-H(18)	0.9500
C(19)-C(41)	1.378(4)
C(19)-C(31)	1.381(4)
C(19)-H(19)	0.9500
C(20)-C(35)	1.383(4)
C(20)-C(21)	1.386(4)
C(20)-H(20)	0.9500
C(21)-C(34)	1.406(4)
C(21)-H(21)	0.9500
C(22)-C(28)	1.396(4)
C(22)-H(22)	0.9500
C(24)-H(24)	0.9500
C(26)-C(29)	1.394(4)
C(26)-H(26)	0.9500
C(28)-H(28)	0.9500
C(29)-C(33)	1.380(4)
C(29)-H(29)	0.9500
C(30)-C(50)	1.386(4)
C(30)-H(30)	0.9500
C(31)-C(43)	1.386(4)
C(31)-H(31)	0.9500
C(32)-C(40)	1.531(4)
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33)	0.9500
C(35)-C(54)	1.388(4)
C(35)-H(35)	0.9500
C(36)-C(51)	1.377(4)
C(36)-C(39)	1.391(4)
C(36)-H(36)	0.9500
C(37)-C(42)	1.383(4)
C(37)-H(37)	0.9500
C(38)-H(38A)	0.9800

C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-H(39)	0.9500
C(40)-C(48)	1.531(3)
C(40)-H(40)	1.0000
C(41)-H(41)	0.9500
C(43)-H(43)	0.9500
O-C(58)	1.396(4)
O-C(55)	1.445(4)
C(45)-C(47)	1.383(4)
C(45)-C(61)	1.392(4)
C(45)-H(45)	0.9500
C(46)-H(46)	0.9500
C(47)-C(49)	1.392(4)
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-C(52)	1.377(4)
C(49)-H(49)	0.9500
C(50)-H(50)	0.9500
C(51)-C(53)	1.383(4)
C(51)-H(51)	0.9500
C(52)-C(60)	1.377(5)
C(52)-H(52)	0.9500
C(53)-H(53)	0.9500
C(54)-H(54)	0.9500
C(59)-H(59A)	0.9800
C(59)-H(59B)	0.9800
C(59)-H(59C)	0.9800
C(55)-C(56)	1.479(5)
C(55)-H(55A)	0.9900
C(55)-H(55B)	0.9900
C(57)-C(58)	1.474(5)
C(57)-H(57A)	0.9800
C(57)-H(57B)	0.9800
C(57)-H(57C)	0.9800
C(58)-H(58A)	0.9900
C(58)-H(58B)	0.9900
C(56)-H(56A)	0.9800
C(56)-H(56B)	0.9800
C(56)-H(56C)	0.9800
C(60)-C(61)	1.374(5)
C(60)-H(60)	0.9500
C(61)-H(61)	0.9500

N-Cu-P(3)	121.39(6)
N-Cu-P(1)	82.24(7)
P(3)-Cu-P(1)	116.44(3)
N-Cu-P(2)	108.01(6)
P(3)-Cu-P(2)	110.41(3)
P(1)-Cu-P(2)	115.91(3)
C(42)-P(1)-C(10)	104.17(12)
C(42)-P(1)-C(40)	102.72(12)
C(10)-P(1)-C(40)	102.35(12)
C(42)-P(1)-Cu	97.24(9)
C(10)-P(1)-Cu	131.56(10)

C(40)-P(1)-Cu	114.63(9)
C(25)-P(2)-C(47)	101.78(12)
C(25)-P(2)-C(4)	100.38(12)
C(47)-P(2)-C(4)	103.50(13)
C(25)-P(2)-Cu	110.60(9)
C(47)-P(2)-Cu	113.75(9)
C(4)-P(2)-Cu	123.95(9)
C(14)-P(3)-C(1)	101.95(12)
C(14)-P(3)-C(23)	103.70(12)
C(1)-P(3)-C(23)	101.64(12)
C(14)-P(3)-Cu	113.42(8)
C(1)-P(3)-Cu	116.43(9)
C(23)-P(3)-Cu	117.61(9)
C(2)-C(1)-C(41)	118.3(2)
C(2)-C(1)-P(3)	118.4(2)
C(41)-C(1)-P(3)	123.3(2)
C(1)-C(2)-C(43)	121.2(3)
C(1)-C(2)-H(2)	119.4
C(43)-C(2)-H(2)	119.4
C(26)-C(3)-C(25)	120.7(3)
C(26)-C(3)-H(3)	119.7
C(25)-C(3)-H(3)	119.7
C(17)-C(4)-C(39)	118.4(2)
C(17)-C(4)-P(2)	120.0(2)
C(39)-C(4)-P(2)	121.6(2)
N-C(5)-C(46)	124.3(2)
N-C(5)-C(42)	119.0(2)
C(46)-C(5)-C(42)	116.5(2)
C(37)-C(6)-C(11)	119.3(3)
C(37)-C(6)-H(6)	120.3
C(11)-C(6)-H(6)	120.3
C(24)-C(7)-C(18)	120.6(3)
C(24)-C(7)-H(7)	119.7
C(18)-C(7)-H(7)	119.7
C(12)-C(8)-C(23)	120.8(2)
C(12)-C(8)-H(8)	119.6
C(23)-C(8)-H(8)	119.6
C(33)-C(9)-C(25)	120.2(3)
C(33)-C(9)-H(9)	119.9
C(25)-C(9)-H(9)	119.9
C(5)-N-C(34)	120.7(2)
C(5)-N-Cu	118.34(16)
C(34)-N-Cu	120.84(17)
C(13)-C(10)-C(38)	110.7(2)
C(13)-C(10)-P(1)	112.18(19)
C(38)-C(10)-P(1)	110.17(18)
C(13)-C(10)-H(10)	107.9
C(38)-C(10)-H(10)	107.9
P(1)-C(10)-H(10)	107.9
C(46)-C(11)-C(6)	119.5(2)
C(46)-C(11)-C(59)	120.2(3)
C(6)-C(11)-C(59)	120.3(3)
C(24)-C(12)-C(8)	120.3(3)
C(24)-C(12)-H(12)	119.8
C(8)-C(12)-H(12)	119.8
C(10)-C(13)-H(13A)	109.5

C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(50)-C(14)-C(28)	118.0(3)
C(50)-C(14)-P(3)	120.9(2)
C(28)-C(14)-P(3)	120.9(2)
C(54)-C(15)-C(34)	121.7(3)
C(54)-C(15)-H(15)	119.2
C(34)-C(15)-H(15)	119.2
C(22)-C(16)-C(30)	119.1(3)
C(22)-C(16)-H(16)	120.4
C(30)-C(16)-H(16)	120.4
C(4)-C(17)-C(53)	121.0(2)
C(4)-C(17)-H(17)	119.5
C(53)-C(17)-H(17)	119.5
C(7)-C(18)-C(23)	120.3(3)
C(7)-C(18)-H(18)	119.9
C(23)-C(18)-H(18)	119.9
C(41)-C(19)-C(31)	120.5(3)
C(41)-C(19)-H(19)	119.7
C(31)-C(19)-H(19)	119.7
C(35)-C(20)-C(21)	121.5(3)
C(35)-C(20)-H(20)	119.2
C(21)-C(20)-H(20)	119.2
C(20)-C(21)-C(34)	120.8(3)
C(20)-C(21)-H(21)	119.6
C(34)-C(21)-H(21)	119.6
C(16)-C(22)-C(28)	120.5(3)
C(16)-C(22)-H(22)	119.8
C(28)-C(22)-H(22)	119.8
C(18)-C(23)-C(8)	118.5(2)
C(18)-C(23)-P(3)	123.6(2)
C(8)-C(23)-P(3)	117.94(19)
C(12)-C(24)-C(7)	119.6(2)
C(12)-C(24)-H(24)	120.2
C(7)-C(24)-H(24)	120.2
C(3)-C(25)-C(9)	118.5(3)
C(3)-C(25)-P(2)	116.9(2)
C(9)-C(25)-P(2)	124.5(2)
C(3)-C(26)-C(29)	120.4(3)
C(3)-C(26)-H(26)	119.8
C(29)-C(26)-H(26)	119.8
C(14)-C(28)-C(22)	120.7(3)
C(14)-C(28)-H(28)	119.7
C(22)-C(28)-H(28)	119.7
C(33)-C(29)-C(26)	119.1(3)
C(33)-C(29)-H(29)	120.4
C(26)-C(29)-H(29)	120.4
C(16)-C(30)-C(50)	120.6(3)
C(16)-C(30)-H(30)	119.7
C(50)-C(30)-H(30)	119.7
C(19)-C(31)-C(43)	119.7(3)
C(19)-C(31)-H(31)	120.2
C(43)-C(31)-H(31)	120.2

C(40)-C(32)-H(32A)	109.5
C(40)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(40)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(9)-C(33)-C(29)	121.0(3)
C(9)-C(33)-H(33)	119.5
C(29)-C(33)-H(33)	119.5
N-C(34)-C(15)	118.6(2)
N-C(34)-C(21)	124.3(2)
C(15)-C(34)-C(21)	116.8(2)
C(20)-C(35)-C(54)	118.3(3)
C(20)-C(35)-H(35)	120.9
C(54)-C(35)-H(35)	120.9
C(51)-C(36)-C(39)	120.6(3)
C(51)-C(36)-H(36)	119.7
C(39)-C(36)-H(36)	119.7
C(42)-C(37)-C(6)	121.9(2)
C(42)-C(37)-H(37)	119.0
C(6)-C(37)-H(37)	119.0
C(10)-C(38)-H(38A)	109.5
C(10)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(10)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(36)-C(39)-C(4)	120.2(3)
C(36)-C(39)-H(39)	119.9
C(4)-C(39)-H(39)	119.9
C(48)-C(40)-C(32)	110.7(2)
C(48)-C(40)-P(1)	110.14(18)
C(32)-C(40)-P(1)	113.78(18)
C(48)-C(40)-H(40)	107.3
C(32)-C(40)-H(40)	107.3
P(1)-C(40)-H(40)	107.3
C(19)-C(41)-C(1)	120.8(3)
C(19)-C(41)-H(41)	119.6
C(1)-C(41)-H(41)	119.6
C(37)-C(42)-C(5)	120.2(2)
C(37)-C(42)-P(1)	124.8(2)
C(5)-C(42)-P(1)	115.0(2)
C(31)-C(43)-C(2)	119.6(3)
C(31)-C(43)-H(43)	120.2
C(2)-C(43)-H(43)	120.2
C(58)-O-C(55)	113.7(3)
C(47)-C(45)-C(61)	120.1(3)
C(47)-C(45)-H(45)	120.0
C(61)-C(45)-H(45)	120.0
C(11)-C(46)-C(5)	122.5(2)
C(11)-C(46)-H(46)	118.7
C(5)-C(46)-H(46)	118.7
C(45)-C(47)-C(49)	118.5(3)
C(45)-C(47)-P(2)	124.2(2)
C(49)-C(47)-P(2)	117.1(2)
C(40)-C(48)-H(48A)	109.5

C(40)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(40)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(52)-C(49)-C(47)	121.7(3)
C(52)-C(49)-H(49)	119.1
C(47)-C(49)-H(49)	119.1
C(30)-C(50)-C(14)	121.2(3)
C(30)-C(50)-H(50)	119.4
C(14)-C(50)-H(50)	119.4
C(36)-C(51)-C(53)	119.8(3)
C(36)-C(51)-H(51)	120.1
C(53)-C(51)-H(51)	120.1
C(60)-C(52)-C(49)	118.8(3)
C(60)-C(52)-H(52)	120.6
C(49)-C(52)-H(52)	120.6
C(51)-C(53)-C(17)	120.1(3)
C(51)-C(53)-H(53)	120.0
C(17)-C(53)-H(53)	120.0
C(15)-C(54)-C(35)	120.9(3)
C(15)-C(54)-H(54)	119.6
C(35)-C(54)-H(54)	119.6
C(11)-C(59)-H(59A)	109.5
C(11)-C(59)-H(59B)	109.5
H(59A)-C(59)-H(59B)	109.5
C(11)-C(59)-H(59C)	109.5
H(59A)-C(59)-H(59C)	109.5
H(59B)-C(59)-H(59C)	109.5
O-C(55)-C(56)	111.3(3)
O-C(55)-H(55A)	109.4
C(56)-C(55)-H(55A)	109.4
O-C(55)-H(55B)	109.4
C(56)-C(55)-H(55B)	109.4
H(55A)-C(55)-H(55B)	108.0
C(58)-C(57)-H(57A)	109.5
C(58)-C(57)-H(57B)	109.5
H(57A)-C(57)-H(57B)	109.5
C(58)-C(57)-H(57C)	109.5
H(57A)-C(57)-H(57C)	109.5
H(57B)-C(57)-H(57C)	109.5
O-C(58)-C(57)	107.0(3)
O-C(58)-H(58A)	110.3
C(57)-C(58)-H(58A)	110.3
O-C(58)-H(58B)	110.3
C(57)-C(58)-H(58B)	110.3
H(58A)-C(58)-H(58B)	108.6
C(55)-C(56)-H(56A)	109.5
C(55)-C(56)-H(56B)	109.5
H(56A)-C(56)-H(56B)	109.5
C(55)-C(56)-H(56C)	109.5
H(56A)-C(56)-H(56C)	109.5
H(56B)-C(56)-H(56C)	109.5
C(61)-C(60)-C(52)	120.9(3)
C(61)-C(60)-H(60)	119.6
C(52)-C(60)-H(60)	119.6

C(60)-C(61)-C(45)	120.0(3)
C(60)-C(61)-H(61)	120.0
C(45)-C(61)-H(61)	120.0

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $^{Me}PNCu(PPh_3)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu	13(1)	14(1)	11(1)	0(1)	3(1)	1(1)
P(1)	12(1)	13(1)	12(1)	-1(1)	4(1)	2(1)
P(2)	14(1)	13(1)	12(1)	0(1)	3(1)	0(1)
P(3)	13(1)	13(1)	11(1)	1(1)	2(1)	1(1)
C(1)	16(1)	11(1)	13(1)	0(1)	-2(1)	1(1)
C(2)	27(2)	22(2)	20(2)	4(1)	8(1)	6(1)
C(3)	23(2)	17(1)	20(2)	-2(1)	5(1)	2(1)
C(4)	18(1)	15(1)	9(2)	0(1)	1(1)	3(1)
C(5)	14(1)	14(1)	10(2)	-4(1)	0(1)	-4(1)
C(6)	19(2)	23(2)	19(2)	-1(1)	11(1)	-3(1)
C(7)	26(2)	15(1)	34(2)	-6(1)	4(1)	-5(1)
C(8)	20(1)	14(1)	17(2)	-1(1)	7(1)	-2(1)
C(9)	20(2)	17(1)	23(2)	-4(1)	8(1)	0(1)
N	13(1)	14(1)	12(1)	1(1)	6(1)	0(1)
C(10)	16(1)	22(1)	15(2)	0(1)	6(1)	4(1)
C(11)	26(2)	15(1)	14(2)	-1(1)	4(1)	-5(1)
C(12)	14(1)	26(2)	16(2)	1(1)	4(1)	1(1)
C(13)	19(2)	29(2)	26(2)	2(1)	8(1)	8(1)
C(14)	17(1)	12(1)	12(2)	2(1)	8(1)	1(1)
C(15)	18(2)	15(1)	15(2)	1(1)	2(1)	0(1)
C(16)	36(2)	31(2)	23(2)	-5(1)	15(2)	4(1)
C(17)	19(2)	15(1)	16(2)	0(1)	2(1)	-2(1)
C(18)	21(2)	18(1)	21(2)	-1(1)	5(1)	0(1)
C(19)	36(2)	19(2)	19(2)	5(1)	3(1)	-2(1)
C(20)	18(2)	22(2)	22(2)	5(1)	-4(1)	-1(1)
C(21)	20(2)	19(1)	13(2)	0(1)	5(1)	1(1)
C(22)	20(2)	34(2)	29(2)	-1(2)	9(1)	6(1)
C(23)	11(1)	19(1)	12(2)	-4(1)	6(1)	-3(1)
C(24)	17(2)	31(2)	17(2)	-9(1)	2(1)	-5(1)
C(25)	16(1)	14(1)	18(2)	-4(1)	7(1)	-1(1)
C(26)	35(2)	22(2)	27(2)	5(1)	15(2)	3(1)
C(28)	20(2)	26(2)	17(2)	-2(1)	3(1)	1(1)
C(29)	28(2)	23(2)	44(2)	-1(2)	25(2)	-5(1)
C(30)	31(2)	28(2)	13(2)	-1(1)	3(1)	4(1)
C(31)	42(2)	19(2)	30(2)	6(1)	5(2)	13(1)
C(32)	18(2)	21(1)	17(2)	-6(1)	4(1)	0(1)
C(33)	15(2)	23(2)	36(2)	-7(1)	10(1)	-2(1)
C(34)	15(1)	9(1)	16(2)	0(1)	4(1)	0(1)
C(35)	13(2)	23(2)	37(2)	5(1)	5(1)	3(1)
C(36)	35(2)	16(1)	27(2)	-6(1)	12(2)	-2(1)
C(37)	13(1)	21(1)	16(2)	-6(1)	5(1)	0(1)
C(38)	11(1)	31(2)	23(2)	-3(1)	1(1)	2(1)
C(39)	20(2)	18(1)	25(2)	-3(1)	9(1)	-3(1)
C(40)	20(1)	13(1)	14(2)	-3(1)	6(1)	0(1)

C(41)	19(2)	19(1)	20(2)	-1(1)	5(1)	0(1)
C(42)	14(1)	15(1)	9(2)	-2(1)	-3(1)	-2(1)
C(43)	38(2)	29(2)	30(2)	3(2)	11(2)	16(2)
O	69(2)	42(2)	42(2)	-9(1)	11(1)	5(1)
C(45)	28(2)	29(2)	18(2)	2(1)	4(1)	-3(1)
C(46)	15(1)	16(1)	13(2)	-1(1)	5(1)	-1(1)
C(47)	13(1)	21(1)	18(2)	5(1)	3(1)	-2(1)
C(48)	18(2)	25(2)	17(2)	-6(1)	6(1)	-4(1)
C(49)	25(2)	28(2)	22(2)	7(1)	10(1)	5(1)
C(50)	18(1)	17(1)	20(2)	-1(1)	4(1)	2(1)
C(51)	35(2)	20(2)	20(2)	-1(1)	11(1)	9(1)
C(52)	36(2)	39(2)	37(2)	17(2)	14(2)	21(2)
C(53)	17(2)	28(2)	20(2)	1(1)	7(1)	4(1)
C(54)	24(2)	20(1)	26(2)	0(1)	16(1)	4(1)
C(59)	35(2)	26(2)	26(2)	7(1)	13(2)	2(1)
C(55)	42(2)	46(2)	51(3)	-5(2)	28(2)	-4(2)
C(57)	99(3)	37(2)	39(2)	7(2)	30(2)	12(2)
C(58)	82(3)	39(2)	71(3)	-13(2)	39(3)	-15(2)
C(56)	57(3)	41(2)	55(3)	-4(2)	22(2)	-6(2)
C(60)	30(2)	58(2)	38(2)	24(2)	5(2)	19(2)
C(61)	37(2)	58(2)	20(2)	4(2)	-3(2)	-4(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $^{Me}PNCu(PPh_3)_2$.

	x	y	z	U(eq)
H(2)	1410	5714	2678	27
H(3)	1309	2874	3075	24
H(6)	115	3153	5012	23
H(7)	6190	6677	3595	31
H(8)	5416	4547	3461	20
H(9)	-1373	3341	1537	23
H(10)	-808	4834	3780	21
H(12)	7071	4936	4223	23
H(13A)	-739	5444	2631	36
H(13B)	-363	5774	3303	36
H(13C)	-1762	5552	3026	36
H(15)	4284	3380	2812	19
H(16)	5481	4065	577	34
H(17)	3687	3524	1712	20
H(18)	4560	6293	2811	24
H(19)	2631	6852	1120	30
H(20)	6944	3418	4800	27
H(21)	4856	3631	4692	21
H(22)	6676	4101	1606	33
H(24)	7432	6001	4310	26
H(26)	-116	2281	3439	32
H(28)	5867	4533	2402	26
H(29)	-2186	2223	2864	35
H(30)	3457	4448	351	29
H(31)	958	7192	1504	37
H(32A)	1076	5034	4812	28

H(32B)	298	5567	4384	28
H(32C)	1589	5732	4861	28
H(33)	-2785	2747	1911	29
H(35)	7731	3190	3929	29
H(36)	1800	1611	1112	30
H(37)	-234	4033	4373	20
H(38A)	-2220	4362	2972	33
H(38B)	-1054	3903	3148	33
H(38C)	-1245	4335	2539	33
H(39)	763	2359	1567	25
H(40)	1794	5664	3807	19
H(41)	3669	5944	1498	23
H(43)	372	6634	2303	38
H(45)	251	3387	676	30
H(46)	3316	2842	4487	17
H(48A)	3575	5486	4604	29
H(48B)	3615	5053	4016	29
H(48C)	3247	4763	4619	29
H(49)	290	4836	1849	29
H(50)	2629	4857	1144	22
H(51)	3769	1811	964	29
H(52)	-960	5408	1044	44
H(53)	4704	2773	1252	26
H(54)	6371	3177	2932	26
H(59A)	1965	2461	5660	42
H(59B)	2846	2185	5245	42
H(59C)	1397	2024	5072	42
H(55A)	4444	3632	8957	52
H(55B)	4448	4358	9119	52
H(57A)	2188	3350	10174	84
H(57B)	1409	2825	9733	84
H(57C)	1072	3543	9598	84
H(58A)	3299	2973	9466	72
H(58B)	2184	3183	8892	72
H(56A)	2528	3823	8189	74
H(56B)	3746	4108	8025	74
H(56C)	2832	4547	8295	74
H(60)	-1626	4960	54	51
H(61)	-1002	3965	-137	48

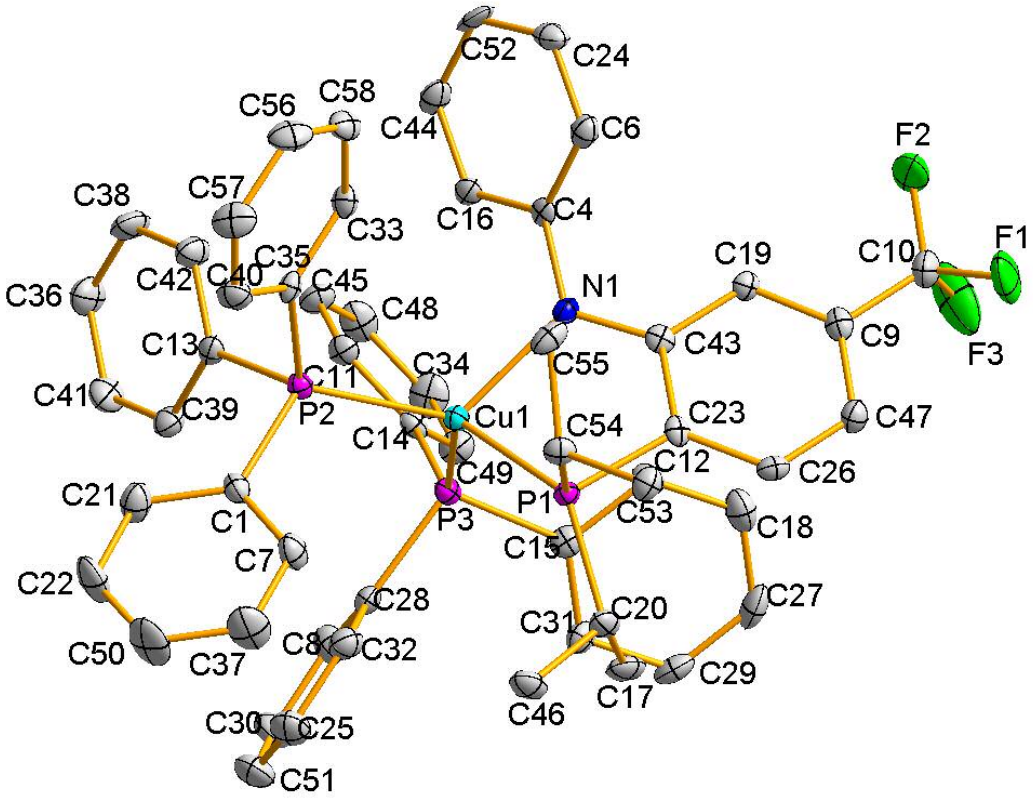

Figure S28. Fully numbered molecular structure of **8**. Hydrogen atoms omitted for clarity.

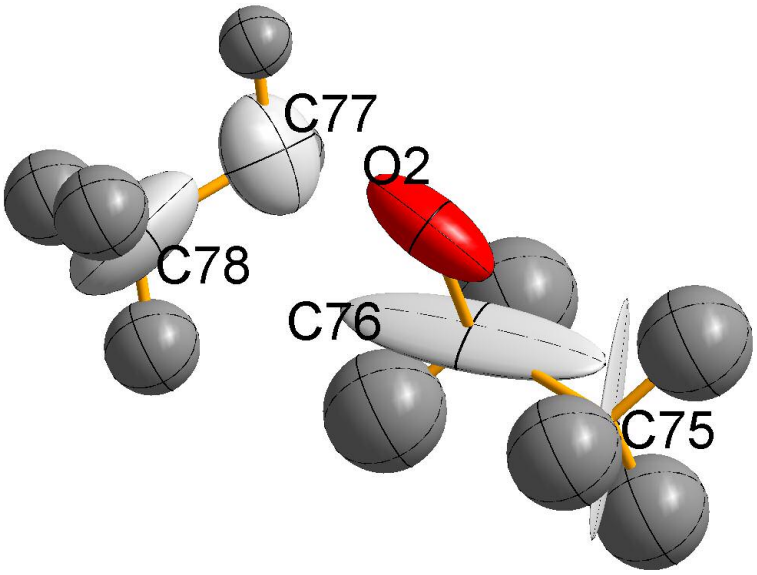

Figure S29. Highly disordered diethyl ether molecule crystallized with **8**.

$^{CF3}PNCu(PPh_3)_2$ (**8**)

Table 1. Crystal data and structure refinement for $^{CF3}PNCu(PPh_3)_2$.

Identification code	$^{CF3}PNCu(PPh_3)_2$	
Empirical formula	C59 H62 Cu F3 N O P3	
Formula weight	1014.55	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.101(16) Å	α= 90°.
	b = 21.70(5) Å	β= 103.11(7)°.
	c = 22.30(4) Å	γ = 90°.
Volume	5231(17) Å^3	
Z	4	
Density (calculated)	1.288 Mg/m^3	
Absorption coefficient	0.561 mm^{-1}	
F(000)	2128	
Crystal size	0.296 x 0.0518 x 0.037 mm^3	
Theta range for data collection	1.88 to 28.30°.	
Index ranges	-14≤h≤14, -28≤k≤28, -29≤l≤28	
Reflections collected	59030	
Independent reflections	11900 [R(int) = 0.1305]	
Completeness to theta = 28.30°	91.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11900 / 0 / 619	
Goodness-of-fit on F^2	1.320	
Final R indices [I>2σ(I)]	R1 = 0.0617, wR2 = 0.1007	
R indices (all data)	R1 = 0.1176, wR2 = 0.1078	
Largest diff. peak and hole	1.541 and -1.180 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $^{CF3}PNCu(PPh_3)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	7353(1)	4340(1)	2853(1)	14(1)
P(2)	8523(1)	5077(1)	2481(1)	13(1)
P(3)	6334(1)	3682(1)	2053(1)	15(1)
P(1)	6114(1)	4696(1)	3505(1)	13(1)
N(1)	8107(3)	3795(1)	3621(1)	15(1)
C(1)	7696(3)	5779(2)	2137(2)	17(1)
F(3)	6316(3)	1918(1)	4906(1)	63(1)
F(2)	8102(2)	2258(1)	5355(1)	58(1)
C(4)	9339(3)	3583(1)	3729(2)	12(1)
F(1)	6532(2)	2490(1)	5704(1)	46(1)
C(6)	10165(3)	3574(2)	4316(2)	18(1)
C(7)	6776(3)	6014(2)	2406(2)	22(1)
C(8)	4966(3)	3874(2)	809(2)	24(1)
C(9)	6715(3)	2984(2)	4776(2)	16(1)
C(10)	6916(4)	2422(2)	5175(2)	26(1)
C(11)	8310(3)	3177(2)	1607(2)	17(1)
C(12)	5525(3)	2879(2)	2845(2)	20(1)
C(13)	9218(3)	4791(2)	1856(2)	16(1)

C(14)	7114(3)	3076(2)	1688(2)	15(1)
C(15)	5155(3)	3207(2)	2293(2)	17(1)
C(16)	9832(3)	3425(2)	3222(2)	17(1)
C(17)	3686(3)	4370(2)	2957(2)	25(1)
C(18)	4703(4)	2508(2)	3064(2)	28(1)
C(19)	7569(3)	3139(2)	4436(1)	14(1)
C(20)	4439(3)	4879(2)	3349(2)	19(1)
C(21)	7983(4)	6099(2)	1648(2)	26(1)
C(22)	7346(4)	6636(2)	1429(2)	34(1)
C(23)	6287(3)	4015(2)	4004(1)	14(1)
C(24)	11403(3)	3421(2)	4378(2)	22(1)
C(25)	4408(4)	5093(2)	1047(2)	30(1)
C(26)	5430(3)	3838(2)	4351(2)	16(1)
C(27)	3474(4)	2468(2)	2736(2)	28(1)
C(28)	5422(3)	4122(2)	1398(2)	17(1)
C(29)	3098(3)	2789(2)	2188(2)	23(1)
C(30)	4227(4)	4237(2)	347(2)	33(1)
C(31)	3926(3)	3161(2)	1965(2)	18(1)
C(32)	5139(3)	4739(2)	1505(2)	23(1)
C(33)	10582(3)	5015(2)	3472(2)	18(1)
C(34)	7155(4)	2066(2)	1215(2)	27(1)
C(35)	9846(3)	5410(2)	3042(2)	14(1)
C(36)	10206(4)	4263(2)	914(2)	29(1)
C(37)	6154(4)	6559(2)	2187(2)	36(1)
C(38)	10912(3)	4307(2)	1505(2)	30(1)
C(39)	8491(3)	4734(2)	1252(2)	20(1)
C(40)	10116(3)	6044(2)	3084(2)	22(1)
C(41)	8988(3)	4479(2)	785(2)	26(1)
C(42)	10422(3)	4567(2)	1976(2)	24(1)
C(43)	7377(3)	3657(2)	4022(1)	13(1)
C(44)	11066(3)	3279(2)	3289(2)	21(1)
C(45)	8919(3)	2728(2)	1336(2)	23(1)
C(46)	4142(3)	5510(2)	3042(2)	23(1)
C(47)	5626(3)	3323(2)	4734(2)	19(1)
C(48)	8348(4)	2178(2)	1138(2)	26(1)
C(49)	6543(3)	2514(2)	1491(2)	22(1)
C(50)	6437(4)	6868(2)	1702(2)	38(1)
C(51)	3955(4)	4840(2)	469(2)	34(1)
C(52)	11871(3)	3281(2)	3866(2)	25(1)
C(53)	6124(3)	5444(2)	4572(2)	19(1)
C(54)	6819(3)	5320(2)	4059(2)	16(1)
C(55)	8191(3)	5171(2)	4345(2)	21(1)
C(56)	11800(4)	5870(2)	3968(2)	26(1)
C(57)	11083(3)	6273(2)	3541(2)	26(1)
C(58)	11558(3)	5242(2)	3930(2)	20(1)
O(2)	7864(4)	3820(2)	9440(2)	87(1)
C(75)	6505(9)	3217(3)	9751(3)	160(5)
C(77)	8785(6)	3964(3)	8951(3)	80(2)
C(76)	7548(8)	3295(3)	9352(5)	228(8)
C(78)	8178(6)	4097(3)	8370(4)	110(3)

Table 3. Bond lengths [Å] and angles [°] for $^{CF3}PNCu(PPh_3)_2$.

Cu(1)-N(1)	2.091(4)

Cu(1)-P(2)	2.328(3)
Cu(1)-P(1)	2.347(3)
Cu(1)-P(3)	2.363(3)
P(2)-C(13)	1.846(4)
P(2)-C(35)	1.848(4)
P(2)-C(1)	1.853(5)
P(3)-C(15)	1.839(4)
P(3)-C(28)	1.844(4)
P(3)-C(14)	1.861(4)
P(1)-C(23)	1.834(5)
P(1)-C(20)	1.855(4)
P(1)-C(54)	1.879(4)
N(1)-C(43)	1.369(4)
N(1)-C(4)	1.411(4)
C(1)-C(21)	1.390(5)
C(1)-C(7)	1.393(5)
F(3)-C(10)	1.348(5)
F(2)-C(10)	1.334(4)
C(4)-C(16)	1.406(5)
C(4)-C(6)	1.417(5)
F(1)-C(10)	1.349(4)
C(6)-C(24)	1.390(5)
C(6)-H(6)	0.9500
C(7)-C(37)	1.401(5)
C(7)-H(7)	0.9500
C(8)-C(28)	1.403(5)
C(8)-C(30)	1.405(5)
C(8)-H(8)	0.9500
C(9)-C(19)	1.382(5)
C(9)-C(47)	1.401(5)
C(9)-C(10)	1.496(5)
C(11)-C(14)	1.398(5)
C(11)-C(45)	1.399(5)
C(11)-H(11)	0.9500
C(12)-C(18)	1.388(5)
C(12)-C(15)	1.399(5)
C(12)-H(12)	0.9500
C(13)-C(42)	1.391(5)
C(13)-C(39)	1.410(5)
C(14)-C(49)	1.398(5)
C(15)-C(31)	1.398(5)
C(16)-C(44)	1.381(5)
C(16)-H(16)	0.9500
C(17)-C(20)	1.533(5)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(27)	1.397(5)
C(18)-H(18)	0.9500
C(19)-C(43)	1.440(5)
C(19)-H(19)	0.9500
C(20)-C(46)	1.533(5)
C(20)-H(20)	1.0000
C(21)-C(22)	1.393(5)
C(21)-H(21)	0.9500
C(22)-C(50)	1.387(6)

C(22)-H(22)	0.9500
C(23)-C(26)	1.409(5)
C(23)-C(43)	1.431(5)
C(24)-C(52)	1.390(5)
C(24)-H(24)	0.9500
C(25)-C(32)	1.384(5)
C(25)-C(51)	1.386(6)
C(25)-H(25)	0.9500
C(26)-C(47)	1.393(5)
C(26)-H(26)	0.9500
C(27)-C(29)	1.386(5)
C(27)-H(27)	0.9500
C(28)-C(32)	1.409(6)
C(29)-C(31)	1.398(5)
C(29)-H(29)	0.9500
C(30)-C(51)	1.382(6)
C(30)-H(30)	0.9500
C(31)-H(31)	0.9500
C(32)-H(32)	0.9500
C(33)-C(58)	1.400(5)
C(33)-C(35)	1.402(5)
C(33)-H(33)	0.9500
C(34)-C(48)	1.396(5)
C(34)-C(49)	1.405(5)
C(34)-H(34)	0.9500
C(35)-C(40)	1.406(5)
C(36)-C(38)	1.375(5)
C(36)-C(41)	1.398(5)
C(36)-H(36)	0.9500
C(37)-C(50)	1.368(6)
C(37)-H(37)	0.9500
C(38)-C(42)	1.406(5)
C(38)-H(38)	0.9500
C(39)-C(41)	1.400(5)
C(39)-H(39)	0.9500
C(40)-C(57)	1.393(5)
C(40)-H(40)	0.9500
C(41)-H(41)	0.9500
C(42)-H(42)	0.9500
C(44)-C(52)	1.390(5)
C(44)-H(44)	0.9500
C(45)-C(48)	1.376(5)
C(45)-H(45)	0.9500
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-H(47)	0.9500
C(48)-H(48)	0.9500
C(49)-H(49)	0.9500
C(50)-H(50)	0.9500
C(51)-H(51)	0.9500
C(52)-H(52)	0.9500
C(53)-C(54)	1.542(5)
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(53)-H(53C)	0.9800

C(54)-C(55)	1.545(5)
C(54)-H(54)	1.0000
C(55)-H(55A)	0.9800
C(55)-H(55B)	0.9800
C(55)-H(55C)	0.9800
C(56)-C(58)	1.388(6)
C(56)-C(57)	1.400(5)
C(56)-H(56)	0.9500
C(57)-H(57)	0.9500
C(58)-H(58)	0.9500
O(2)-C(76)	1.194(7)
O(2)-C(77)	1.686(7)
C(75)-C(76)	1.621(12)
C(75)-H(75A)	0.9800
C(75)-H(75B)	0.9800
C(75)-H(75C)	0.9800
C(77)-C(78)	1.347(8)
C(77)-H(77A)	0.9900
C(77)-H(77B)	0.9900
C(76)-H(76A)	0.9900
C(76)-H(76B)	0.9900
C(78)-H(78A)	0.9800
C(78)-H(78B)	0.9800
C(78)-H(78C)	0.9800

N(1)-Cu(1)-P(2)	121.87(12)
N(1)-Cu(1)-P(1)	82.08(15)
P(2)-Cu(1)-P(1)	116.54(13)
N(1)-Cu(1)-P(3)	108.08(17)
P(2)-Cu(1)-P(3)	110.84(13)
P(1)-Cu(1)-P(3)	114.76(11)
C(13)-P(2)-C(35)	103.75(19)
C(13)-P(2)-C(1)	102.48(19)
C(35)-P(2)-C(1)	101.6(2)
C(13)-P(2)-Cu(1)	113.65(16)
C(35)-P(2)-Cu(1)	116.71(16)
C(1)-P(2)-Cu(1)	116.68(17)
C(15)-P(3)-C(28)	102.80(19)
C(15)-P(3)-C(14)	99.4(2)
C(28)-P(3)-C(14)	104.2(2)
C(15)-P(3)-Cu(1)	111.68(16)
C(28)-P(3)-Cu(1)	111.59(19)
C(14)-P(3)-Cu(1)	124.55(15)
C(23)-P(1)-C(20)	104.38(17)
C(23)-P(1)-C(54)	102.1(2)
C(20)-P(1)-C(54)	102.70(18)
C(23)-P(1)-Cu(1)	96.57(16)
C(20)-P(1)-Cu(1)	131.14(14)
C(54)-P(1)-Cu(1)	115.39(14)
C(43)-N(1)-C(4)	120.8(3)
C(43)-N(1)-Cu(1)	118.1(2)
C(4)-N(1)-Cu(1)	121.1(2)
C(21)-C(1)-C(7)	118.5(3)
C(21)-C(1)-P(2)	123.8(3)
C(7)-C(1)-P(2)	117.7(3)
C(16)-C(4)-N(1)	118.7(3)

C(16)-C(4)-C(6)	116.8(3)
N(1)-C(4)-C(6)	124.2(3)
C(24)-C(6)-C(4)	120.9(3)
C(24)-C(6)-H(6)	119.5
C(4)-C(6)-H(6)	119.5
C(1)-C(7)-C(37)	120.6(4)
C(1)-C(7)-H(7)	119.7
C(37)-C(7)-H(7)	119.7
C(28)-C(8)-C(30)	119.9(4)
C(28)-C(8)-H(8)	120.1
C(30)-C(8)-H(8)	120.1
C(19)-C(9)-C(47)	121.6(3)
C(19)-C(9)-C(10)	119.8(3)
C(47)-C(9)-C(10)	118.5(3)
F(2)-C(10)-F(3)	105.8(4)
F(2)-C(10)-F(1)	104.6(3)
F(3)-C(10)-F(1)	104.7(3)
F(2)-C(10)-C(9)	113.5(3)
F(3)-C(10)-C(9)	113.9(3)
F(1)-C(10)-C(9)	113.4(3)
C(14)-C(11)-C(45)	120.9(3)
C(14)-C(11)-H(11)	119.6
C(45)-C(11)-H(11)	119.6
C(18)-C(12)-C(15)	121.3(4)
C(18)-C(12)-H(12)	119.4
C(15)-C(12)-H(12)	119.4
C(42)-C(13)-C(39)	118.0(3)
C(42)-C(13)-P(2)	121.4(3)
C(39)-C(13)-P(2)	120.3(3)
C(11)-C(14)-C(49)	118.2(3)
C(11)-C(14)-P(3)	119.7(3)
C(49)-C(14)-P(3)	122.1(3)
C(31)-C(15)-C(12)	118.8(3)
C(31)-C(15)-P(3)	124.2(3)
C(12)-C(15)-P(3)	117.0(3)
C(44)-C(16)-C(4)	121.7(3)
C(44)-C(16)-H(16)	119.1
C(4)-C(16)-H(16)	119.1
C(20)-C(17)-H(17A)	109.5
C(20)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(20)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(12)-C(18)-C(27)	119.6(4)
C(12)-C(18)-H(18)	120.2
C(27)-C(18)-H(18)	120.2
C(9)-C(19)-C(43)	121.5(3)
C(9)-C(19)-H(19)	119.3
C(43)-C(19)-H(19)	119.3
C(46)-C(20)-C(17)	110.8(3)
C(46)-C(20)-P(1)	112.3(2)
C(17)-C(20)-P(1)	110.3(3)
C(46)-C(20)-H(20)	107.8
C(17)-C(20)-H(20)	107.8
P(1)-C(20)-H(20)	107.8

C(1)-C(21)-C(22)	120.3(4)
C(1)-C(21)-H(21)	119.9
C(22)-C(21)-H(21)	119.9
C(50)-C(22)-C(21)	120.8(4)
C(50)-C(22)-H(22)	119.6
C(21)-C(22)-H(22)	119.6
C(26)-C(23)-C(43)	120.6(3)
C(26)-C(23)-P(1)	124.2(3)
C(43)-C(23)-P(1)	115.2(3)
C(6)-C(24)-C(52)	121.0(4)
C(6)-C(24)-H(24)	119.5
C(52)-C(24)-H(24)	119.5
C(32)-C(25)-C(51)	119.7(4)
C(32)-C(25)-H(25)	120.2
C(51)-C(25)-H(25)	120.2
C(47)-C(26)-C(23)	121.6(3)
C(47)-C(26)-H(26)	119.2
C(23)-C(26)-H(26)	119.2
C(29)-C(27)-C(18)	119.6(4)
C(29)-C(27)-H(27)	120.2
C(18)-C(27)-H(27)	120.2
C(8)-C(28)-C(32)	118.4(3)
C(8)-C(28)-P(3)	124.0(3)
C(32)-C(28)-P(3)	117.5(3)
C(27)-C(29)-C(31)	120.9(4)
C(27)-C(29)-H(29)	119.5
C(31)-C(29)-H(29)	119.5
C(51)-C(30)-C(8)	120.2(4)
C(51)-C(30)-H(30)	119.9
C(8)-C(30)-H(30)	119.9
C(29)-C(31)-C(15)	119.8(4)
C(29)-C(31)-H(31)	120.1
C(15)-C(31)-H(31)	120.1
C(25)-C(32)-C(28)	121.2(4)
C(25)-C(32)-H(32)	119.4
C(28)-C(32)-H(32)	119.4
C(58)-C(33)-C(35)	121.2(4)
C(58)-C(33)-H(33)	119.4
C(35)-C(33)-H(33)	119.4
C(48)-C(34)-C(49)	120.0(4)
C(48)-C(34)-H(34)	120.0
C(49)-C(34)-H(34)	120.0
C(33)-C(35)-C(40)	118.1(3)
C(33)-C(35)-P(2)	118.3(3)
C(40)-C(35)-P(2)	123.6(3)
C(38)-C(36)-C(41)	119.2(4)
C(38)-C(36)-H(36)	120.4
C(41)-C(36)-H(36)	120.4
C(50)-C(37)-C(7)	120.4(4)
C(50)-C(37)-H(37)	119.8
C(7)-C(37)-H(37)	119.8
C(36)-C(38)-C(42)	120.8(4)
C(36)-C(38)-H(38)	119.6
C(42)-C(38)-H(38)	119.6
C(41)-C(39)-C(13)	120.6(4)
C(41)-C(39)-H(39)	119.7

C(13)-C(39)-H(39)	119.7
C(57)-C(40)-C(35)	121.0(3)
C(57)-C(40)-H(40)	119.5
C(35)-C(40)-H(40)	119.5
C(36)-C(41)-C(39)	120.4(3)
C(36)-C(41)-H(41)	119.8
C(39)-C(41)-H(41)	119.8
C(13)-C(42)-C(38)	121.0(4)
C(13)-C(42)-H(42)	119.5
C(38)-C(42)-H(42)	119.5
N(1)-C(43)-C(23)	119.0(3)
N(1)-C(43)-C(19)	124.5(3)
C(23)-C(43)-C(19)	116.3(3)
C(16)-C(44)-C(52)	121.0(4)
C(16)-C(44)-H(44)	119.5
C(52)-C(44)-H(44)	119.5
C(48)-C(45)-C(11)	120.6(4)
C(48)-C(45)-H(45)	119.7
C(11)-C(45)-H(45)	119.7
C(20)-C(46)-H(46A)	109.5
C(20)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(20)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(26)-C(47)-C(9)	118.3(3)
C(26)-C(47)-H(47)	120.8
C(9)-C(47)-H(47)	120.8
C(45)-C(48)-C(34)	119.5(4)
C(45)-C(48)-H(48)	120.2
C(34)-C(48)-H(48)	120.2
C(14)-C(49)-C(34)	120.8(4)
C(14)-C(49)-H(49)	119.6
C(34)-C(49)-H(49)	119.6
C(37)-C(50)-C(22)	119.4(4)
C(37)-C(50)-H(50)	120.3
C(22)-C(50)-H(50)	120.3
C(30)-C(51)-C(25)	120.6(4)
C(30)-C(51)-H(51)	119.7
C(25)-C(51)-H(51)	119.7
C(44)-C(52)-C(24)	118.6(4)
C(44)-C(52)-H(52)	120.7
C(24)-C(52)-H(52)	120.7
C(54)-C(53)-H(53A)	109.5
C(54)-C(53)-H(53B)	109.5
H(53A)-C(53)-H(53B)	109.5
C(54)-C(53)-H(53C)	109.5
H(53A)-C(53)-H(53C)	109.5
H(53B)-C(53)-H(53C)	109.5
C(53)-C(54)-C(55)	110.0(3)
C(53)-C(54)-P(1)	114.2(3)
C(55)-C(54)-P(1)	110.2(2)
C(53)-C(54)-H(54)	107.4
C(55)-C(54)-H(54)	107.4
P(1)-C(54)-H(54)	107.4
C(54)-C(55)-H(55A)	109.5

C(54)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5
C(54)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(58)-C(56)-C(57)	119.9(4)
C(58)-C(56)-H(56)	120.0
C(57)-C(56)-H(56)	120.0
C(40)-C(57)-C(56)	120.0(4)
C(40)-C(57)-H(57)	120.0
C(56)-C(57)-H(57)	120.0
C(56)-C(58)-C(33)	119.9(4)
C(56)-C(58)-H(58)	120.1
C(33)-C(58)-H(58)	120.1
C(76)-O(2)-C(77)	105.6(7)
C(76)-C(75)-H(75A)	109.5
C(76)-C(75)-H(75B)	109.5
H(75A)-C(75)-H(75B)	109.5
C(76)-C(75)-H(75C)	109.5
H(75A)-C(75)-H(75C)	109.5
H(75B)-C(75)-H(75C)	109.5
C(78)-C(77)-O(2)	114.6(6)
C(78)-C(77)-H(77A)	108.6
O(2)-C(77)-H(77A)	108.6
C(78)-C(77)-H(77B)	108.6
O(2)-C(77)-H(77B)	108.6
H(77A)-C(77)-H(77B)	107.6
O(2)-C(76)-C(75)	103.3(8)
O(2)-C(76)-H(76A)	111.1
C(75)-C(76)-H(76A)	111.1
O(2)-C(76)-H(76B)	111.1
C(75)-C(76)-H(76B)	111.1
H(76A)-C(76)-H(76B)	109.1
C(77)-C(78)-H(78A)	109.5
C(77)-C(78)-H(78B)	109.5
H(78A)-C(78)-H(78B)	109.5
C(77)-C(78)-H(78C)	109.5
H(78A)-C(78)-H(78C)	109.5
H(78B)-C(78)-H(78C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $^{CF3}PNCu(PPh_3)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	14(1)	15(1)	14(1)	2(1)	4(1)	2(1)
P(2)	14(1)	12(1)	13(1)	1(1)	4(1)	1(1)
P(3)	16(1)	15(1)	14(1)	0(1)	3(1)	2(1)
P(1)	12(1)	13(1)	13(1)	0(1)	3(1)	2(1)
N(1)	13(2)	18(2)	14(2)	-1(1)	5(1)	-1(1)
C(1)	20(2)	17(2)	14(2)	3(2)	2(2)	-2(2)
F(3)	111(3)	24(2)	47(2)	7(1)	2(2)	-26(2)
F(2)	39(2)	64(2)	77(2)	51(2)	29(2)	29(1)

C(4)	15(2)	4(2)	17(2)	1(2)	5(2)	0(2)
F(1)	62(2)	52(2)	33(1)	21(1)	31(1)	17(1)
C(6)	20(2)	15(2)	23(2)	1(2)	9(2)	0(2)
C(7)	28(2)	23(2)	16(2)	2(2)	8(2)	4(2)
C(8)	29(2)	19(2)	23(2)	1(2)	3(2)	-4(2)
C(9)	21(2)	13(2)	14(2)	-2(2)	3(2)	-5(2)
C(10)	25(2)	32(3)	22(2)	6(2)	10(2)	-1(2)
C(11)	18(2)	12(2)	21(2)	-1(2)	5(2)	1(2)
C(12)	21(2)	21(2)	18(2)	0(2)	2(2)	0(2)
C(13)	17(2)	13(2)	19(2)	2(2)	8(2)	2(2)
C(14)	19(2)	13(2)	11(2)	0(2)	2(2)	2(2)
C(15)	18(2)	13(2)	18(2)	-6(2)	4(2)	-1(2)
C(16)	16(2)	13(2)	21(2)	3(2)	6(2)	2(2)
C(17)	14(2)	35(2)	25(2)	0(2)	5(2)	10(2)
C(18)	38(3)	22(2)	26(2)	6(2)	10(2)	1(2)
C(19)	16(2)	15(2)	12(2)	-3(2)	5(2)	1(2)
C(20)	17(2)	23(2)	19(2)	1(2)	7(2)	7(2)
C(21)	30(2)	22(2)	28(2)	1(2)	15(2)	2(2)
C(22)	51(3)	21(2)	29(2)	13(2)	11(2)	8(2)
C(23)	18(2)	14(2)	8(2)	-3(2)	3(2)	-3(2)
C(24)	16(2)	21(2)	26(2)	4(2)	-3(2)	-1(2)
C(25)	30(3)	27(2)	34(2)	6(2)	8(2)	11(2)
C(26)	12(2)	18(2)	17(2)	-3(2)	2(2)	2(2)
C(27)	30(3)	23(2)	39(3)	1(2)	22(2)	-6(2)
C(28)	13(2)	21(2)	18(2)	3(2)	6(2)	-1(2)
C(29)	12(2)	25(2)	33(2)	-6(2)	6(2)	-1(2)
C(30)	31(3)	42(3)	22(2)	9(2)	-3(2)	1(2)
C(31)	19(2)	20(2)	18(2)	-2(2)	7(2)	-1(2)
C(32)	19(2)	25(2)	24(2)	0(2)	6(2)	2(2)
C(33)	20(2)	14(2)	19(2)	0(2)	6(2)	-4(2)
C(34)	36(3)	14(2)	32(2)	-8(2)	11(2)	-3(2)
C(35)	16(2)	13(2)	13(2)	-3(2)	7(2)	-3(2)
C(36)	28(2)	38(3)	22(2)	-2(2)	12(2)	5(2)
C(37)	46(3)	29(3)	37(3)	2(2)	19(2)	18(2)
C(38)	16(2)	44(3)	30(2)	2(2)	9(2)	10(2)
C(39)	16(2)	22(2)	21(2)	-1(2)	4(2)	-2(2)
C(40)	19(2)	18(2)	26(2)	2(2)	3(2)	4(2)
C(41)	27(2)	33(3)	15(2)	-2(2)	1(2)	-2(2)
C(42)	19(2)	33(2)	20(2)	0(2)	6(2)	5(2)
C(43)	16(2)	11(2)	10(2)	-5(2)	1(2)	-1(2)
C(44)	21(2)	17(2)	30(2)	1(2)	14(2)	5(2)
C(45)	18(2)	26(2)	28(2)	1(2)	9(2)	5(2)
C(46)	22(2)	24(2)	23(2)	2(2)	4(2)	11(2)
C(47)	19(2)	20(2)	19(2)	0(2)	8(2)	-1(2)
C(48)	38(3)	19(2)	25(2)	-2(2)	13(2)	9(2)
C(49)	21(2)	20(2)	25(2)	-3(2)	6(2)	-1(2)
C(50)	56(3)	17(2)	44(3)	12(2)	17(2)	16(2)
C(51)	31(3)	36(3)	32(3)	13(2)	3(2)	11(2)
C(52)	8(2)	23(2)	46(3)	5(2)	11(2)	4(2)
C(53)	20(2)	18(2)	20(2)	-3(2)	8(2)	-2(2)
C(54)	17(2)	15(2)	18(2)	-2(2)	4(2)	2(2)
C(55)	16(2)	27(2)	23(2)	-9(2)	8(2)	-4(2)
C(56)	19(2)	32(3)	25(2)	-8(2)	-3(2)	-1(2)
C(57)	24(2)	17(2)	35(2)	-8(2)	1(2)	-4(2)
C(58)	19(2)	29(2)	12(2)	-1(2)	2(2)	3(2)
O(2)	90(3)	82(3)	64(3)	-33(2)	-33(2)	42(3)

C(75)	380(13)	55(4)	120(5)	68(4)	213(8)	119(6)
C(77)	94(5)	87(5)	66(4)	-14(4)	32(4)	28(4)
C(76)	142(8)	55(5)	391(17)	-131(8)	-141(9)	38(5)
C(78)	119(7)	67(5)	172(8)	-4(5)	93(6)	-20(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $^{CF3}PNCu(PPh_3)_2$.

	x	y	z	U(eq)
H(6)	9869	3674	4671	22
H(7)	6568	5802	2742	26
H(8)	5157	3461	723	29
H(11)	8715	3555	1737	20
H(12)	6356	2912	3073	24
H(16)	9302	3418	2822	20
H(17A)	2808	4421	2955	37
H(17B)	3970	3966	3131	37
H(17C)	3800	4396	2534	37
H(18)	4974	2282	3436	34
H(19)	8298	2899	4477	17
H(20)	4191	4890	3753	23
H(21)	8617	5951	1461	31
H(22)	7537	6846	1088	40
H(24)	11938	3413	4776	27
H(25)	4217	5507	1128	36
H(26)	4701	4075	4324	19
H(27)	2900	2222	2887	34
H(29)	2266	2756	1961	28
H(30)	3913	4069	-51	39
H(31)	3655	3383	1591	22
H(32)	5455	4916	1899	27
H(33)	10416	4585	3451	21
H(34)	6756	1686	1081	32
H(36)	10543	4088	597	34
H(37)	5531	6715	2376	43
H(38)	11740	4160	1596	35
H(39)	7656	4870	1162	24
H(40)	9632	6320	2796	26
H(41)	8495	4451	378	31
H(42)	10921	4589	2382	28
H(44)	11369	3176	2936	26
H(45)	9735	2803	1288	28
H(46A)	4350	5507	2638	35
H(46B)	4627	5828	3301	35
H(46C)	3258	5597	2991	35
H(47)	5036	3205	4962	22
H(48)	8764	1876	950	32
H(49)	5733	2434	1545	27
H(50)	6014	7238	1554	46
H(51)	3454	5082	154	41
H(52)	12723	3188	3910	30
H(53A)	6041	5058	4788	29

H(53B)	5301	5609	4390	29
H(53C)	6589	5743	4865	29
H(54)	6798	5709	3817	20
H(55A)	8590	5532	4570	32
H(55B)	8612	5066	4017	32
H(55C)	8241	4823	4629	32
H(56)	12451	6027	4284	32
H(57)	11256	6702	3563	32
H(58)	12054	4968	4215	24
H(75A)	5832	3511	9604	240
H(75B)	6875	3296	10186	240
H(75C)	6176	2796	9703	240
H(77A)	9334	4314	9113	97
H(77B)	9316	3599	8940	97
H(76A)	8250	3011	9499	274
H(76B)	7196	3218	8909	274
H(78A)	7527	3790	8230	165
H(78B)	8760	4089	8099	165
H(78C)	7806	4507	8360	165

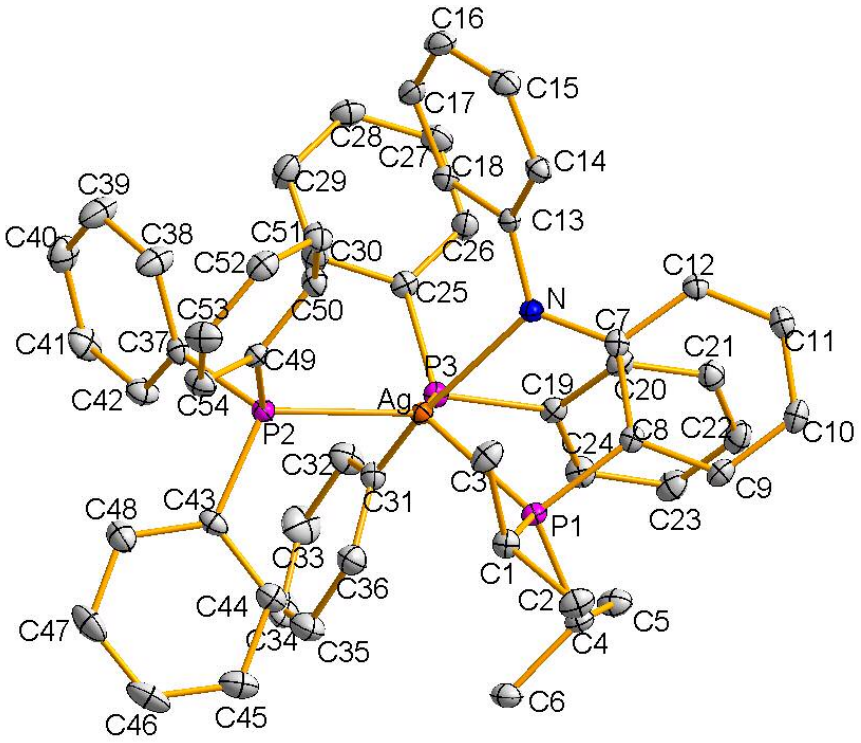

Figure S30. Fully numbered molecular structure of **9**. Hydrogen atoms omitted for clarity.

PNAg(PPh_3)$_2$ (**9**)

Table 1. Crystal data and structure refinement for PNAg(PPh_3)$_2$.

Identification code	$PNAg(PPh_3)_2$	
Empirical formula	C54 H53 Ag N P3	
Formula weight	916.75	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.8189(5) Å	α= 90°.
	b = 19.1162(8) Å	β= 97.2540(10)°.
	c = 22.2135(9) Å	γ = 90°.
Volume	4557.3(3) $Å^3$	
Z	4	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	0.585 mm^{-1}	
F(000)	1904	
Crystal size	0.370 x 0.222 x 0.185 mm^3	
Theta range for data collection	1.41 to 35.99°.	
Index ranges	$-16\leq h\leq 17$, $-31\leq k\leq 31$, $-35\leq l\leq 30$	
Reflections collected	80341	
Independent reflections	19574 [R(int) = 0.0665]	
Completeness to theta = 35.99°	90.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19574 / 0 / 536	
Goodness-of-fit on F^2	1.446	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0378, wR2 = 0.0629	
R indices (all data)	R1 = 0.0585, wR2 = 0.0662	
Largest diff. peak and hole	1.912 and -0.672 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $PNAg(PPh_3)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ag(1)	1581(1)	7437(1)	858(1)	12(1)
C(1)	2604(1)	6150(1)	-209(1)	16(1)
C(2)	3553(1)	5639(1)	-417(1)	21(1)
C(3)	1368(1)	5784(1)	-141(1)	21(1)
C(4)	4775(1)	6879(1)	419(1)	15(1)
C(5)	5384(1)	7215(1)	1008(1)	21(1)
C(6)	4821(1)	7371(1)	-124(1)	20(1)
C(7)	2308(1)	5924(1)	1470(1)	13(1)
C(8)	3296(1)	5978(1)	1101(1)	13(1)
C(9)	4357(1)	5552(1)	1219(1)	16(1)
C(10)	4492(1)	5067(1)	1687(1)	19(1)
C(11)	3528(1)	5003(1)	2047(1)	18(1)
C(12)	2468(1)	5412(1)	1943(1)	15(1)
C(13)	224(1)	6250(1)	1628(1)	13(1)
C(14)	-354(1)	5587(1)	1616(1)	16(1)
C(15)	-1536(1)	5501(1)	1785(1)	21(1)
C(16)	-2206(1)	6071(1)	1969(1)	23(1)
C(17)	-1645(1)	6723(1)	1991(1)	20(1)
C(18)	-457(1)	6815(1)	1831(1)	16(1)
C(19)	3702(1)	7936(1)	2151(1)	14(1)
C(20)	3624(1)	7249(1)	2360(1)	16(1)

C(21)	4651(1)	6931(1)	2691(1)	19(1)
C(22)	5773(1)	7289(1)	2804(1)	21(1)
C(23)	5865(1)	7968(1)	2587(1)	21(1)
C(24)	4836(1)	8293(1)	2268(1)	18(1)
C(25)	1268(1)	8515(1)	2222(1)	14(1)
C(26)	1460(1)	8346(1)	2836(1)	20(1)
C(27)	553(2)	8494(1)	3210(1)	25(1)
C(28)	-546(1)	8822(1)	2977(1)	22(1)
C(29)	-745(2)	8995(1)	2365(1)	25(1)
C(30)	147(1)	8836(1)	1991(1)	22(1)
C(31)	2866(1)	9134(1)	1427(1)	16(1)
C(32)	2898(2)	9739(1)	1783(1)	24(1)
C(33)	3344(2)	10361(1)	1569(1)	32(1)
C(34)	3760(2)	10388(1)	1005(1)	33(1)
C(35)	3729(2)	9794(1)	648(1)	30(1)
C(36)	3268(1)	9170(1)	857(1)	22(1)
C(37)	-1124(1)	8581(1)	346(1)	14(1)
C(38)	-2251(1)	8431(1)	556(1)	24(1)
C(39)	-2932(2)	8951(1)	807(1)	30(1)
C(40)	-2492(2)	9630(1)	842(1)	26(1)
C(41)	-1381(2)	9788(1)	629(1)	24(1)
C(42)	-692(1)	9271(1)	387(1)	20(1)
C(43)	373(1)	8229(1)	-592(1)	16(1)
C(44)	1591(1)	8089(1)	-698(1)	19(1)
C(45)	2019(2)	8302(1)	-1235(1)	26(1)
C(46)	1227(2)	8651(1)	-1670(1)	29(1)
C(47)	16(2)	8808(1)	-1568(1)	28(1)
C(48)	-411(2)	8603(1)	-1030(1)	22(1)
C(49)	-1245(1)	7189(1)	-158(1)	13(1)
C(50)	-1474(1)	6694(1)	275(1)	17(1)
C(51)	-2254(1)	6128(1)	123(1)	20(1)
C(52)	-2819(1)	6050(1)	-470(1)	19(1)
C(53)	-2620(1)	6543(1)	-900(1)	22(1)
C(54)	-1831(1)	7113(1)	-750(1)	20(1)
N(1)	1333(1)	6388(1)	1397(1)	13(1)
P(1)	3152(1)	6636(1)	503(1)	12(1)
P(2)	-137(1)	7882(1)	102(1)	13(1)
P(3)	2339(1)	8287(1)	1680(1)	13(1)

Table 3. Bond lengths [Å] and angles [°] for $PNAg(PPh_3)_2$.

Ag(1)-N(1)	2.3688(11)
Ag(1)-P(1)	2.4881(4)
Ag(1)-P(2)	2.4919(4)
Ag(1)-P(3)	2.5028(4)
C(1)-C(2)	1.5304(19)
C(1)-C(3)	1.5333(19)
C(1)-P(1)	1.8647(14)
C(1)-H(1)	1.0000
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800

C(3)-H(3C)	0.9800
C(4)-C(5)	1.529(2)
C(4)-C(6)	1.536(2)
C(4)-P(1)	1.8484(13)
C(4)-H(4)	1.0000
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-N(1)	1.3718(17)
C(7)-C(12)	1.4290(19)
C(7)-C(8)	1.4313(19)
C(8)-C(9)	1.4059(18)
C(8)-P(1)	1.8215(14)
C(9)-C(10)	1.387(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.398(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.3830(19)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-N(1)	1.3886(17)
C(13)-C(18)	1.4126(19)
C(13)-C(14)	1.4127(18)
C(14)-C(15)	1.388(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.398(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.385(2)
C(16)-H(16)	0.9500
C(17)-C(18)	1.386(2)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(20)	1.3990(18)
C(19)-C(24)	1.3994(19)
C(19)-P(3)	1.8250(14)
C(20)-C(21)	1.392(2)
C(20)-H(20)	0.9500
C(21)-C(22)	1.388(2)
C(21)-H(21)	0.9500
C(22)-C(23)	1.392(2)
C(22)-H(22)	0.9500
C(23)-C(24)	1.389(2)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
C(25)-C(26)	1.394(2)
C(25)-C(30)	1.398(2)
C(25)-P(3)	1.8262(14)
C(26)-C(27)	1.391(2)
C(26)-H(26)	0.9500
C(27)-C(28)	1.385(2)
C(27)-H(27)	0.9500
C(28)-C(29)	1.388(2)
C(28)-H(28)	0.9500

C(29)-C(30)	1.385(2)
C(29)-H(29)	0.9500
C(30)-H(30)	0.9500
C(31)-C(36)	1.391(2)
C(31)-C(32)	1.398(2)
C(31)-P(3)	1.8284(14)
C(32)-C(33)	1.390(2)
C(32)-H(32)	0.9500
C(33)-C(34)	1.384(3)
C(33)-H(33)	0.9500
C(34)-C(35)	1.384(3)
C(34)-H(34)	0.9500
C(35)-C(36)	1.395(2)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
C(37)-C(38)	1.389(2)
C(37)-C(42)	1.3981(18)
C(37)-P(2)	1.8335(14)
C(38)-C(39)	1.395(2)
C(38)-H(38)	0.9500
C(39)-C(40)	1.381(2)
C(39)-H(39)	0.9500
C(40)-C(41)	1.381(2)
C(40)-H(40)	0.9500
C(41)-C(42)	1.388(2)
C(41)-H(41)	0.9500
C(42)-H(42)	0.9500
C(43)-C(44)	1.394(2)
C(43)-C(48)	1.403(2)
C(43)-P(2)	1.8271(14)
C(44)-C(45)	1.394(2)
C(44)-H(44)	0.9500
C(45)-C(46)	1.380(2)
C(45)-H(45)	0.9500
C(46)-C(47)	1.390(2)
C(46)-H(46)	0.9500
C(47)-C(48)	1.391(2)
C(47)-H(47)	0.9500
C(48)-H(48)	0.9500
C(49)-C(50)	1.3935(19)
C(49)-C(54)	1.3951(19)
C(49)-P(2)	1.8313(13)
C(50)-C(51)	1.3873(19)
C(50)-H(50)	0.9500
C(51)-C(52)	1.388(2)
C(51)-H(51)	0.9500
C(52)-C(53)	1.378(2)
C(52)-H(52)	0.9500
C(53)-C(54)	1.398(2)
C(53)-H(53)	0.9500
C(54)-H(54)	0.9500

N(1)-Ag(1)-P(1)	76.40(3)
N(1)-Ag(1)-P(2)	120.48(3)
P(1)-Ag(1)-P(2)	118.529(12)
N(1)-Ag(1)-P(3)	103.22(3)

P(1)-Ag(1)-P(3)	117.168(12)
P(2)-Ag(1)-P(3)	114.666(12)
C(2)-C(1)-C(3)	111.44(11)
C(2)-C(1)-P(1)	114.89(10)
C(3)-C(1)-P(1)	109.41(10)
C(2)-C(1)-H(1)	106.9
C(3)-C(1)-H(1)	106.9
P(1)-C(1)-H(1)	106.9
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(5)-C(4)-C(6)	111.20(11)
C(5)-C(4)-P(1)	109.38(10)
C(6)-C(4)-P(1)	110.96(10)
C(5)-C(4)-H(4)	108.4
C(6)-C(4)-H(4)	108.4
P(1)-C(4)-H(4)	108.4
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
N(1)-C(7)-C(12)	123.34(12)
N(1)-C(7)-C(8)	120.21(12)
C(12)-C(7)-C(8)	116.20(12)
C(9)-C(8)-C(7)	120.11(12)
C(9)-C(8)-P(1)	121.97(11)
C(7)-C(8)-P(1)	117.87(9)
C(10)-C(9)-C(8)	122.29(13)
C(10)-C(9)-H(9)	118.9
C(8)-C(9)-H(9)	118.9
C(9)-C(10)-C(11)	118.15(13)
C(9)-C(10)-H(10)	120.9
C(11)-C(10)-H(10)	120.9
C(12)-C(11)-C(10)	121.18(13)
C(12)-C(11)-H(11)	119.4
C(10)-C(11)-H(11)	119.4
C(11)-C(12)-C(7)	122.06(13)
C(11)-C(12)-H(12)	119.0
C(7)-C(12)-H(12)	119.0

N(1)-C(13)-C(18)	118.93(12)
N(1)-C(13)-C(14)	124.31(12)
C(18)-C(13)-C(14)	116.41(12)
C(15)-C(14)-C(13)	121.43(13)
C(15)-C(14)-H(14)	119.3
C(13)-C(14)-H(14)	119.3
C(14)-C(15)-C(16)	121.13(13)
C(14)-C(15)-H(15)	119.4
C(16)-C(15)-H(15)	119.4
C(17)-C(16)-C(15)	118.05(14)
C(17)-C(16)-H(16)	121.0
C(15)-C(16)-H(16)	121.0
C(16)-C(17)-C(18)	121.43(14)
C(16)-C(17)-H(17)	119.3
C(18)-C(17)-H(17)	119.3
C(17)-C(18)-C(13)	121.51(13)
C(17)-C(18)-H(18)	119.2
C(13)-C(18)-H(18)	119.2
C(20)-C(19)-C(24)	119.00(13)
C(20)-C(19)-P(3)	117.17(10)
C(24)-C(19)-P(3)	123.59(10)
C(21)-C(20)-C(19)	120.46(13)
C(21)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8
C(22)-C(21)-C(20)	120.14(13)
C(22)-C(21)-H(21)	119.9
C(20)-C(21)-H(21)	119.9
C(21)-C(22)-C(23)	119.70(13)
C(21)-C(22)-H(22)	120.2
C(23)-C(22)-H(22)	120.2
C(24)-C(23)-C(22)	120.43(13)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(23)-C(24)-C(19)	120.24(13)
C(23)-C(24)-H(24)	119.9
C(19)-C(24)-H(24)	119.9
C(26)-C(25)-C(30)	118.46(13)
C(26)-C(25)-P(3)	124.20(11)
C(30)-C(25)-P(3)	117.18(11)
C(27)-C(26)-C(25)	120.49(13)
C(27)-C(26)-H(26)	119.8
C(25)-C(26)-H(26)	119.8
C(28)-C(27)-C(26)	120.44(15)
C(28)-C(27)-H(27)	119.8
C(26)-C(27)-H(27)	119.8
C(27)-C(28)-C(29)	119.54(14)
C(27)-C(28)-H(28)	120.2
C(29)-C(28)-H(28)	120.2
C(30)-C(29)-C(28)	120.13(14)
C(30)-C(29)-H(29)	119.9
C(28)-C(29)-H(29)	119.9
C(29)-C(30)-C(25)	120.93(14)
C(29)-C(30)-H(30)	119.5
C(25)-C(30)-H(30)	119.5
C(36)-C(31)-C(32)	119.03(13)
C(36)-C(31)-P(3)	117.91(10)

C(32)-C(31)-P(3)	123.06(11)
C(33)-C(32)-C(31)	120.01(16)
C(33)-C(32)-H(32)	120.0
C(31)-C(32)-H(32)	120.0
C(34)-C(33)-C(32)	120.47(16)
C(34)-C(33)-H(33)	119.8
C(32)-C(33)-H(33)	119.8
C(33)-C(34)-C(35)	120.10(15)
C(33)-C(34)-H(34)	119.9
C(35)-C(34)-H(34)	119.9
C(34)-C(35)-C(36)	119.63(16)
C(34)-C(35)-H(35)	120.2
C(36)-C(35)-H(35)	120.2
C(31)-C(36)-C(35)	120.74(15)
C(31)-C(36)-H(36)	119.6
C(35)-C(36)-H(36)	119.6
C(38)-C(37)-C(42)	118.28(13)
C(38)-C(37)-P(2)	121.12(10)
C(42)-C(37)-P(2)	120.23(11)
C(37)-C(38)-C(39)	121.17(14)
C(37)-C(38)-H(38)	119.4
C(39)-C(38)-H(38)	119.4
C(40)-C(39)-C(38)	119.79(15)
C(40)-C(39)-H(39)	120.1
C(38)-C(39)-H(39)	120.1
C(41)-C(40)-C(39)	119.67(14)
C(41)-C(40)-H(40)	120.2
C(39)-C(40)-H(40)	120.2
C(40)-C(41)-C(42)	120.72(14)
C(40)-C(41)-H(41)	119.6
C(42)-C(41)-H(41)	119.6
C(41)-C(42)-C(37)	120.37(14)
C(41)-C(42)-H(42)	119.8
C(37)-C(42)-H(42)	119.8
C(44)-C(43)-C(48)	118.82(13)
C(44)-C(43)-P(2)	117.73(11)
C(48)-C(43)-P(2)	123.40(11)
C(43)-C(44)-C(45)	120.79(14)
C(43)-C(44)-H(44)	119.6
C(45)-C(44)-H(44)	119.6
C(46)-C(45)-C(44)	119.73(16)
C(46)-C(45)-H(45)	120.1
C(44)-C(45)-H(45)	120.1
C(45)-C(46)-C(47)	120.37(15)
C(45)-C(46)-H(46)	119.8
C(47)-C(46)-H(46)	119.8
C(46)-C(47)-C(48)	120.03(15)
C(46)-C(47)-H(47)	120.0
C(48)-C(47)-H(47)	120.0
C(47)-C(48)-C(43)	120.20(15)
C(47)-C(48)-H(48)	119.9
C(43)-C(48)-H(48)	119.9
C(50)-C(49)-C(54)	118.79(12)
C(50)-C(49)-P(2)	116.09(10)
C(54)-C(49)-P(2)	125.09(10)
C(51)-C(50)-C(49)	121.09(13)

C(51)-C(50)-H(50)	119.5
C(49)-C(50)-H(50)	119.5
C(50)-C(51)-C(52)	119.78(13)
C(50)-C(51)-H(51)	120.1
C(52)-C(51)-H(51)	120.1
C(53)-C(52)-C(51)	119.74(13)
C(53)-C(52)-H(52)	120.1
C(51)-C(52)-H(52)	120.1
C(52)-C(53)-C(54)	120.80(14)
C(52)-C(53)-H(53)	119.6
C(54)-C(53)-H(53)	119.6
C(49)-C(54)-C(53)	119.77(13)
C(49)-C(54)-H(54)	120.1
C(53)-C(54)-H(54)	120.1
C(7)-N(1)-C(13)	121.44(11)
C(7)-N(1)-Ag(1)	118.23(9)
C(13)-N(1)-Ag(1)	120.33(8)
C(8)-P(1)-C(4)	104.56(6)
C(8)-P(1)-C(1)	105.18(6)
C(4)-P(1)-C(1)	104.16(6)
C(8)-P(1)-Ag(1)	101.10(4)
C(4)-P(1)-Ag(1)	124.95(4)
C(1)-P(1)-Ag(1)	114.79(4)
C(43)-P(2)-C(49)	104.56(6)
C(43)-P(2)-C(37)	103.52(6)
C(49)-P(2)-C(37)	103.77(6)
C(43)-P(2)-Ag(1)	114.44(5)
C(49)-P(2)-Ag(1)	111.60(4)
C(37)-P(2)-Ag(1)	117.58(5)
C(19)-P(3)-C(25)	104.09(6)
C(19)-P(3)-C(31)	103.95(6)
C(25)-P(3)-C(31)	103.82(6)
C(19)-P(3)-Ag(1)	110.28(4)
C(25)-P(3)-Ag(1)	117.33(4)
C(31)-P(3)-Ag(1)	115.93(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $PNAg(PPh_3)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag(1)	11(1)	11(1)	12(1)	0(1)	1(1)	0(1)
C(1)	17(1)	15(1)	15(1)	-2(1)	1(1)	0(1)
C(2)	21(1)	20(1)	21(1)	-8(1)	5(1)	-2(1)
C(3)	16(1)	22(1)	25(1)	-7(1)	1(1)	-2(1)
C(4)	12(1)	18(1)	16(1)	-2(1)	3(1)	-2(1)
C(5)	17(1)	26(1)	19(1)	-3(1)	2(1)	-6(1)
C(6)	18(1)	24(1)	19(1)	2(1)	6(1)	-4(1)
C(7)	14(1)	10(1)	14(1)	-2(1)	0(1)	-1(1)
C(8)	13(1)	12(1)	14(1)	-2(1)	0(1)	0(1)
C(9)	13(1)	17(1)	19(1)	-3(1)	3(1)	1(1)
C(10)	16(1)	17(1)	22(1)	-1(1)	-1(1)	4(1)
C(11)	20(1)	15(1)	17(1)	2(1)	-2(1)	1(1)

C(12)	15(1)	14(1)	16(1)	0(1)	1(1)	-1(1)
C(13)	12(1)	16(1)	12(1)	2(1)	0(1)	0(1)
C(14)	16(1)	16(1)	15(1)	1(1)	1(1)	-2(1)
C(15)	18(1)	25(1)	19(1)	3(1)	0(1)	-7(1)
C(16)	13(1)	37(1)	19(1)	5(1)	4(1)	-3(1)
C(17)	16(1)	28(1)	18(1)	2(1)	4(1)	5(1)
C(18)	15(1)	17(1)	15(1)	1(1)	2(1)	1(1)
C(19)	14(1)	15(1)	12(1)	-3(1)	1(1)	0(1)
C(20)	16(1)	16(1)	17(1)	-3(1)	3(1)	0(1)
C(21)	21(1)	17(1)	19(1)	1(1)	3(1)	3(1)
C(22)	17(1)	26(1)	19(1)	-2(1)	-2(1)	4(1)
C(23)	15(1)	26(1)	21(1)	-4(1)	-1(1)	-3(1)
C(24)	19(1)	17(1)	17(1)	-3(1)	-1(1)	-2(1)
C(25)	15(1)	13(1)	16(1)	-3(1)	2(1)	-1(1)
C(26)	20(1)	22(1)	18(1)	0(1)	2(1)	5(1)
C(27)	30(1)	29(1)	17(1)	3(1)	6(1)	5(1)
C(28)	23(1)	23(1)	22(1)	-4(1)	8(1)	0(1)
C(29)	20(1)	29(1)	24(1)	-4(1)	1(1)	8(1)
C(30)	23(1)	27(1)	15(1)	0(1)	1(1)	8(1)
C(31)	15(1)	15(1)	17(1)	1(1)	0(1)	1(1)
C(32)	30(1)	18(1)	24(1)	-1(1)	6(1)	-3(1)
C(33)	39(1)	15(1)	44(1)	-1(1)	8(1)	-4(1)
C(34)	29(1)	21(1)	48(1)	12(1)	2(1)	-4(1)
C(35)	28(1)	34(1)	29(1)	12(1)	8(1)	-3(1)
C(36)	22(1)	21(1)	21(1)	1(1)	4(1)	0(1)
C(37)	14(1)	14(1)	14(1)	1(1)	-1(1)	0(1)
C(38)	21(1)	16(1)	38(1)	-6(1)	10(1)	-4(1)
C(39)	21(1)	26(1)	45(1)	-4(1)	13(1)	0(1)
C(40)	29(1)	20(1)	29(1)	-3(1)	4(1)	6(1)
C(41)	34(1)	12(1)	27(1)	0(1)	6(1)	-2(1)
C(42)	23(1)	17(1)	22(1)	1(1)	6(1)	-4(1)
C(43)	19(1)	15(1)	13(1)	1(1)	2(1)	-5(1)
C(44)	22(1)	18(1)	17(1)	1(1)	3(1)	-2(1)
C(45)	31(1)	26(1)	23(1)	-1(1)	12(1)	-5(1)
C(46)	46(1)	28(1)	16(1)	2(1)	10(1)	-10(1)
C(47)	37(1)	28(1)	16(1)	6(1)	-5(1)	-7(1)
C(48)	22(1)	22(1)	21(1)	5(1)	-2(1)	-4(1)
C(49)	12(1)	14(1)	14(1)	-2(1)	2(1)	0(1)
C(50)	17(1)	17(1)	17(1)	1(1)	-2(1)	-2(1)
C(51)	19(1)	17(1)	23(1)	3(1)	1(1)	-3(1)
C(52)	16(1)	17(1)	23(1)	-5(1)	1(1)	-3(1)
C(53)	22(1)	29(1)	16(1)	-5(1)	0(1)	-8(1)
C(54)	21(1)	22(1)	15(1)	1(1)	1(1)	-5(1)
N(1)	12(1)	13(1)	16(1)	1(1)	3(1)	0(1)
P(1)	11(1)	12(1)	13(1)	-2(1)	2(1)	-1(1)
P(2)	12(1)	13(1)	12(1)	1(1)	0(1)	-2(1)
P(3)	14(1)	12(1)	12(1)	-1(1)	1(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $PNAg(PPh_3)_2$.

	x	y	z	U(eq)
H(1)	2424	6506	-537	19

H(2A)	3797	5297	-95	31
H(2B)	4291	5898	-506	31
H(2C)	3181	5395	-783	31
H(3A)	1041	5563	-527	31
H(3B)	767	6128	-29	31
H(3C)	1506	5425	176	31
H(4)	5245	6443	346	18
H(5A)	6285	7248	1000	31
H(5B)	5217	6927	1354	31
H(5C)	5039	7684	1048	31
H(6A)	4391	7809	-52	30
H(6B)	4409	7148	-493	30
H(6C)	5691	7471	-173	30
H(9)	5005	5598	970	19
H(10)	5220	4786	1761	22
H(11)	3602	4672	2369	21
H(12)	1827	5351	2193	18
H(14)	76	5191	1489	19
H(15)	-1896	5047	1776	25
H(16)	-3023	6012	2076	28
H(17)	-2083	7116	2117	25
H(18)	-93	7268	1859	19
H(20)	2864	6998	2275	19
H(21)	4584	6469	2840	23
H(22)	6475	7071	3028	25
H(23)	6636	8210	2657	25
H(24)	4903	8760	2129	21
H(26)	2216	8127	3002	24
H(27)	688	8369	3627	30
H(28)	-1159	8928	3234	27
H(29)	-1494	9223	2204	29
H(30)	-6	8947	1571	26
H(32)	2614	9724	2170	29
H(33)	3364	10771	1812	39
H(34)	4068	10815	864	39
H(35)	4019	9811	262	36
H(36)	3228	8765	608	26
H(38)	-2562	7966	528	29
H(39)	-3697	8838	952	36
H(40)	-2952	9986	1013	31
H(41)	-1085	10256	648	29
H(42)	78	9386	247	24
H(44)	2136	7846	-400	22
H(45)	2853	8207	-1302	31
H(46)	1510	8785	-2041	35
H(47)	-521	9055	-1867	33
H(48)	-1235	8717	-959	26
H(50)	-1088	6745	682	21
H(51)	-2402	5796	424	24
H(52)	-3340	5658	-578	23
H(53)	-3024	6494	-1303	27
H(54)	-1695	7447	-1051	23

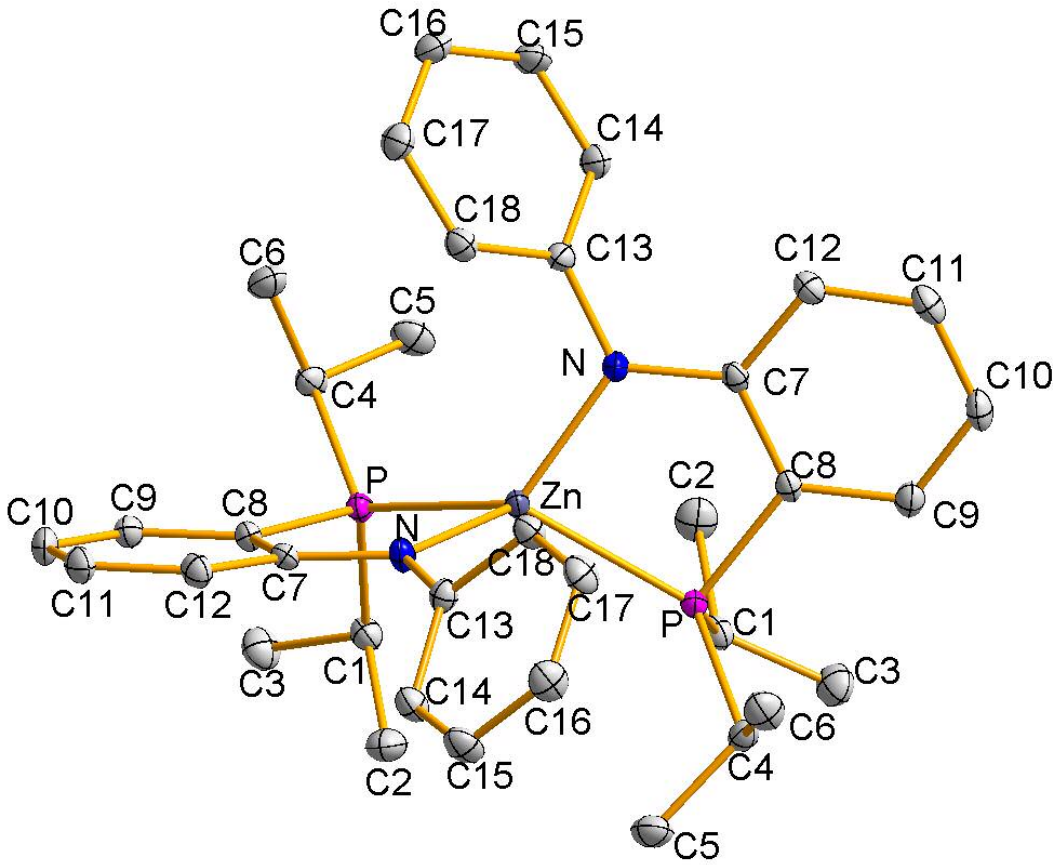

Figure S31. Fully numbered molecular structure of **10**. Hydrogen atoms omitted for clarity.

PN_2Zn (**10**)

Table 1. Crystal data and structure refinement for PN_2Zn.

Identification code	PN_2Zn	
Empirical formula	C36 H46 N2 P2 Zn	
Formula weight	634.06	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 21.074(14) Å	α= 90°.
	b = 8.729(6) Å	β= 110.905(14)°.
	c = 19.086(13) Å	γ = 90°.
Volume	3280(4) $Å^3$	
Z	4	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.873 mm^{-1}	
F(000)	1344	
Crystal size	0.259 x 0.244 x 0.152 mm^3	
Theta range for data collection	2.07 to 38.26°.	
Index ranges	-27≤h≤36, -15≤k≤14, -31≤l≤30	
Reflections collected	26044	

Independent reflections	8084 [R(int) = 0.0681]
Completeness to theta = 38.26°	88.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8084 / 0 / 190
Goodness-of-fit on F^2	1.390
Final R indices [I>2σ(I)]	R1 = 0.0451, wR2 = 0.0713
R indices (all data)	R1 = 0.0791, wR2 = 0.0752
Largest diff. peak and hole	1.765 and -1.040 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for PN_2Zn. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn	0	206(1)	2500	11(1)
P	968(1)	-1117(1)	2455(1)	12(1)
N	22(1)	1322(1)	1613(1)	13(1)
C(8)	1072(1)	29(1)	1719(1)	13(1)
C(7)	566(1)	1162(1)	1377(1)	12(1)
C(5)	1706(1)	-1854(2)	3928(1)	21(1)
C(1)	770(1)	-3103(1)	2100(1)	16(1)
C(18)	-836(1)	3175(1)	1591(1)	16(1)
C(9)	1647(1)	-86(2)	1510(1)	16(1)
C(13)	-548(1)	2204(1)	1202(1)	13(1)
C(4)	1799(1)	-1180(1)	3232(1)	16(1)
C(10)	1738(1)	876(2)	980(1)	19(1)
C(17)	-1438(1)	3952(2)	1217(1)	19(1)
C(15)	-1486(1)	2822(2)	65(1)	20(1)
C(11)	1252(1)	1982(2)	650(1)	18(1)
C(6)	2119(1)	402(2)	3414(1)	22(1)
C(16)	-1764(1)	3791(2)	453(1)	20(1)
C(2)	146(1)	-3078(2)	1375(1)	23(1)
C(14)	-890(1)	2032(2)	428(1)	17(1)
C(12)	678(1)	2128(1)	838(1)	16(1)
C(3)	1353(1)	-3965(2)	1979(1)	23(1)

Table 3. Bond lengths [Å] and angles [°] for PN_2Zn.

Zn-N	1.9685(15)
Zn-N#1	1.9686(15)
Zn-P#1	2.3719(12)
Zn-P	2.3720(13)
P-C(8)	1.8013(15)
P-C(4)	1.8471(16)
P-C(1)	1.8537(17)
N-C(7)	1.3790(17)
N-C(13)	1.4068(17)
C(8)-C(9)	1.4065(17)
C(8)-C(7)	1.4305(18)
C(7)-C(12)	1.4135(18)
C(5)-C(4)	1.529(2)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800

C(5)-H(5C)	0.9800
C(1)-C(3)	1.5271(19)
C(1)-C(2)	1.533(2)
C(1)-H(1)	1.0000
C(18)-C(17)	1.3911(19)
C(18)-C(13)	1.3992(18)
C(18)-H(18)	0.9500
C(9)-C(10)	1.3798(19)
C(9)-H(9)	0.9500
C(13)-C(14)	1.401(2)
C(4)-C(6)	1.522(2)
C(4)-H(4)	1.0000
C(10)-C(11)	1.385(2)
C(10)-H(10)	0.9500
C(17)-C(16)	1.380(2)
C(17)-H(17)	0.9500
C(15)-C(14)	1.3833(19)
C(15)-C(16)	1.3857(19)
C(15)-H(15)	0.9500
C(11)-C(12)	1.3842(19)
C(11)-H(11)	0.9500
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(16)-H(16)	0.9500
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(14)-H(14)	0.9500
C(12)-H(12)	0.9500
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800

N-Zn-N#1	120.69(8)
N-Zn-P#1	123.80(3)
N#1-Zn-P#1	85.72(4)
N-Zn-P	85.72(4)
N#1-Zn-P	123.80(3)
P#1-Zn-P	121.74(5)
C(8)-P-C(4)	107.34(7)
C(8)-P-C(1)	107.93(7)
C(4)-P-C(1)	106.88(6)
C(8)-P-Zn	95.96(5)
C(4)-P-Zn	124.52(6)
C(1)-P-Zn	112.61(5)
C(7)-N-C(13)	121.17(11)
C(7)-N-Zn	120.51(8)
C(13)-N-Zn	118.20(8)
C(9)-C(8)-C(7)	119.87(12)
C(9)-C(8)-P	122.57(10)
C(7)-C(8)-P	117.42(9)
N-C(7)-C(12)	123.43(11)
N-C(7)-C(8)	119.55(11)
C(12)-C(7)-C(8)	116.90(11)
C(4)-C(5)-H(5A)	109.5

C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(3)-C(1)-C(2)	110.34(12)
C(3)-C(1)-P	115.39(10)
C(2)-C(1)-P	108.99(9)
C(3)-C(1)-H(1)	107.3
C(2)-C(1)-H(1)	107.3
P-C(1)-H(1)	107.3
C(17)-C(18)-C(13)	120.81(13)
C(17)-C(18)-H(18)	119.6
C(13)-C(18)-H(18)	119.6
C(10)-C(9)-C(8)	121.55(12)
C(10)-C(9)-H(9)	119.2
C(8)-C(9)-H(9)	119.2
C(18)-C(13)-C(14)	117.86(12)
C(18)-C(13)-N	118.76(12)
C(14)-C(13)-N	122.99(12)
C(6)-C(4)-C(5)	109.51(12)
C(6)-C(4)-P	111.89(9)
C(5)-C(4)-P	109.29(10)
C(6)-C(4)-H(4)	108.7
C(5)-C(4)-H(4)	108.7
P-C(4)-H(4)	108.7
C(9)-C(10)-C(11)	118.92(12)
C(9)-C(10)-H(10)	120.5
C(11)-C(10)-H(10)	120.5
C(16)-C(17)-C(18)	120.78(13)
C(16)-C(17)-H(17)	119.6
C(18)-C(17)-H(17)	119.6
C(14)-C(15)-C(16)	121.20(14)
C(14)-C(15)-H(15)	119.4
C(16)-C(15)-H(15)	119.4
C(12)-C(11)-C(10)	121.26(13)
C(12)-C(11)-H(11)	119.4
C(10)-C(11)-H(11)	119.4
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(17)-C(16)-C(15)	118.77(13)
C(17)-C(16)-H(16)	120.6
C(15)-C(16)-H(16)	120.6
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(15)-C(14)-C(13)	120.58(12)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7

C(11)-C(12)-C(7)	121.50(12)
C(11)-C(12)-H(12)	119.3
C(7)-C(12)-H(12)	119.3
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for PN_2Zn. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn	10(1)	15(1)	10(1)	0	5(1)	0
P	10(1)	14(1)	10(1)	0(1)	4(1)	1(1)
N	12(1)	16(1)	13(1)	2(1)	6(1)	2(1)
C(8)	13(1)	16(1)	11(1)	-1(1)	6(1)	-2(1)
C(7)	12(1)	15(1)	8(1)	-2(1)	4(1)	-2(1)
C(5)	23(1)	24(1)	14(1)	2(1)	3(1)	4(1)
C(1)	19(1)	15(1)	15(1)	0(1)	8(1)	0(1)
C(18)	18(1)	18(1)	13(1)	0(1)	6(1)	1(1)
C(9)	13(1)	20(1)	14(1)	-2(1)	6(1)	0(1)
C(13)	12(1)	13(1)	14(1)	2(1)	5(1)	1(1)
C(4)	12(1)	21(1)	13(1)	-2(1)	3(1)	3(1)
C(10)	16(1)	24(1)	20(1)	-3(1)	11(1)	-3(1)
C(17)	21(1)	18(1)	20(1)	-1(1)	9(1)	5(1)
C(15)	20(1)	26(1)	11(1)	1(1)	2(1)	5(1)
C(11)	22(1)	21(1)	16(1)	0(1)	11(1)	-5(1)
C(6)	17(1)	29(1)	18(1)	-2(1)	3(1)	-6(1)
C(16)	18(1)	23(1)	19(1)	4(1)	4(1)	7(1)
C(2)	21(1)	24(1)	21(1)	-7(1)	5(1)	-5(1)
C(14)	18(1)	19(1)	14(1)	0(1)	7(1)	3(1)
C(12)	18(1)	17(1)	14(1)	2(1)	7(1)	-1(1)
C(3)	25(1)	20(1)	25(1)	-2(1)	12(1)	3(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^{\ 3}$) for PN_2Zn.

	x	y	z	U(eq)
H(5A)	2150	-1965	4329	32
H(5B)	1487	-2859	3807	32
H(5C)	1420	-1168	4096	32
H(1)	643	-3689	2481	19
H(18)	-616	3307	2116	19
H(9)	1980	-843	1740	19
H(4)	2111	-1860	3082	19
H(10)	2128	782	844	22

H(17)	-1628	4600	1491	23
H(15)	-1709	2697	-461	24
H(11)	1313	2654	288	22
H(6A)	1846	1043	3619	33
H(6B)	2138	874	2956	33
H(6C)	2580	307	3784	33
H(16)	-2172	4335	198	24
H(2A)	265	-2598	975	34
H(2B)	-218	-2491	1456	34
H(2C)	-9	-4129	1230	34
H(14)	-711	1367	151	20
H(12)	352	2894	600	19
H(3A)	1211	-5019	1824	34
H(3B)	1748	-3978	2447	34
H(3C)	1474	-3452	1587	34